[Chemical papers]

by

John Hall Gladstone

[A collection of sixty
papers taken from
various periodicals, 1851-83]

Contents.

On a compound Sulphate of
    Potassium & Sodium.

On the relations between the Atomic
    weights of analogous elements.
            Phil. Mag. May '53.

On the Corrosive action of Sugar on
    Iron & other metals.

On Chemical affinity among sub-
    stances in Solution.
            R. Inst. March '54.

On gunpowder & its substitutes.
            R. Inst. May '55

Some experiments illustrative of
    the reciprocal decomposition
    of salts.

On the Chemical action of Water
    on soluble salts.
            J. Chem. Soc. 11, 36.

On Collyrite, & a native Carbonate
    of Alumina & lime.
            Phil. Mag. June '62.

Additional notes on reciprocal de-
composition among salts in
solution.   J. Chem. Soc.

On fogs & fog signals.
                R. Inst. march '63

On Essential Oils. Part I.
                J. Chem. Soc.

Note on Crystallized Glycerine.
                J. Chem. Soc. 1867.

On a law in Chemical Dynamics.
                Proc. R. S. 1871.

On Essential Oils. Part II.
                J. Chem. Soc. 1872.

On the Crystallization of Silver, Gold
    & other metals.
                R. Inst. Feby. '72

On the decomposition of Water by
    Zinc in conjunction with a
    more negative metal.
                Proc. R. S. 1872.

Address to the Chemical Section of
    the British Association. 1872.

The Action of oxygen on Copper Nitrate in a state of tension.
Proc. R. S. 1872.

On an Air Battery.
Proc. R. S. 1873.

Observations on the Nature of the black deposit in the Copper-Zinc Couple.
J. Chem. Soc. 1873.

Researches on the action of the Copper Zinc Couple on organic bodies.

Part I.   J. Chem Soc. May '73
  „ II   „   July „
  „ III   „   Oct. „
  „ IV   „   Inch '74
  „ V   „   May „
  „ VI   „   „   „
  „ VII   „   July „
  „ VIII   „   June '75

The Electrolysis of certain metallic Chlorides.   Phil. Mag. June '75

On the replacement of electro positive
    by electro-negative metals in
    a Voltaic cell.
                    Proc. R. S. 1875

Decomposition of water by the joint
    action of aluminium & of
    aluminium Iodide, Bromide or
    Chloride, including instances
    of reverse action.
                    J. Chem. Soc. 1875.

Notes on the action of the Copper-
    Zinc Couple.
                    Phil. mag. Oct. 1875

The augmentation of the Chemical
    activity of aluminium by
    contact with a more negative
    metal.   Phil. mag. Oct. 1875.

The decomposition of Alcohol & its
    homologues by the joint action
    of aluminium & its halogen
    compounds.
                    J. Chem. Soc. 1876

Methods of Chemical decomposition
as illustrated by water.
R. Inst. May 1876.

Phenomena accompanying the
electrolysis of water with
oxidisable electrodes.
J. Chem. Soc. 1876

The simultaneous action of Iodine
& aluminium upon Ether &
Compound ethers.
J. Chem. Soc. 1876.

Preparation of Copper zinc Couples.
J. Chem. Soc. 1877.

Note on the electrolytic Conduction
of some organic bodies.
Proc. R. S. 1877.

On some points connected with the
Chemical Constituents of the
Solar System.
Phil. Mag. Nov. 1877

An enquiry into the action of the
Copper Zinc Couple on alkaline
oxysalts.
J. Chem. Soc. 1878

Analysis between the action of the
    Copper Zinc couple, & of occluded
    & nascent hydrogen.
            J. Chem. Soc. 1878

Researches on the action of the Copper
    Zinc Couple on organic bodies.
    Part. IX. J. Chem. Soc. 1879

Investigations into the action of
    substances in the nascent &
    occluded Conditions. Hydrogen
    (cont?). J. Chem. Soc. 1879.

On dry Copper Zinc couples and
    analogous agents.
            J. Chem. Soc. 1879

The Aluminium Iodide reaction.
            Proc. R. S. 1880.

Note on Thermal Electrolysis.
            Phil. Mag. June 1881

Aluminium Alcohols.
    Part I. Their preparation by
    means of the Aluminium Iodide
    reaction.
            J. Chem. Soc. 1881.

Alumininm Alcohols.
Part II. Their products of
decomposition by heat.
J. Chem. Soc. 1882.

Laboratory notes.
I. On the action of light & heat
on Cane & invert sugars.
II. On Hydroxylamine.
III. Recovery of Iodine from
organic Iodide residues.
IV. A residual phenomenon of
the Electrolysis of Oil of
Vitriol.
V On alleged tests for Alcohol.
VI Reaction of the Copper Zinc
Couple on Nitric oxide
VII On the reducing action of
spongy lead.
J. Chem. Soc. 1883

Address to the Chemical Section
of the British Association, 1883

36 + 39
39.
28.
3.

From these results the following per-centages were obtained :—

	I.	II.
Carbon . . .	50·36	50·43
Hydrogen . .	4·00	3·78

corresponding to the formula $C_{14} H_6 N_2 O_6$, as may be seen from the comparison of the theoretical and experimental numbers:—

				Theory.	Mean of exp.
14 equivs. of Carbon . .	84	50·60	50·39
6 ... Hydrogen .	6	3·62	3·98
2 ... Nitrogen .	28	16·87	
6 ... Oxygen . .	48	28·91	
		166	100·00	

This body is therefore nitrobenzamide, having the same relation to nitrobenzoate of ammonia as cuminamide has to cuminate of ammonia.

This beautiful substance can only be obtained with difficulty, as the nitrobenzoate of ammonia explodes violently unless very great caution is employed.

A specimen of chlorobenzoic acid, made in the laboratory for some other investigation, was dissolved in ammonia and heated ; it fused readily, became perfectly insoluble in cold water and ammonia, but soluble in hot water, crystallizing as the solution cooled in long needles of great beauty. The specimen of acid afforded me, being all that could be spared, was insufficient for the manufacture of an amide ; I prepared a portion of chlorobenzoic acid by acting upon benzoic acid for some days with hydrochloric acid and chlorate of potash ; after purification it was burnt with chromate of lead and gave the following results :—

I. 0·394 grm.=0·769 of carbonic acid and 0·114 of water.
From this result the following per-centage was obtained :—

	Experiment.	Theory.
Carbon . . .	53·22	53·61
Hydrogen . .	3·22	3·25

leading to the formula $HO, C_{14} \begin{Bmatrix} H_4 \\ Cl \end{Bmatrix} O_3$, 1 equiv. of the hydrogen of benzoic acid replaced by an equivalent of chlorine.

This acid, however, on being subjected to the usual treatment by solution in ammonia and subsequent heat, did not fuse but blackened, charcoal being separated. Unfortunately the specimen of ammoniacal salt from which I had made the former compound was not analysed, probably it would have

proved to be $C_{14}\left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right\} O_3, HO$, or $C_{14}\left\{\begin{matrix} H_2 \\ Cl_3 \end{matrix}\right\} O_3, HO$, a dichlorobenzoic or a trichlorobenzoic acid, such existing.

These experiments were conducted in the laboratories of the Royal College of Chemistry under the direction of Dr. Hofmann, to whom I beg to offer my best thanks for his advice and assistance during their progress.

CCI. *Contributions to the Chemical History of Gun-Cotton and Xyloidine. By* Mr. JOHN HALL GLADSTONE, *of University College, London.*

AT the commencement of the present year, having perceived that considerable doubt rested on the ultimate composition of gun-cotton, I undertook a series of experiments with a view to ascertain it, if possible; and during my investigation my attention was drawn to various papers that appeared on the subject, where I found contradictory accounts, not only of the results of analysis, but also of the action of various reputed solvents. The experiments detailed below, although they are far from exhausting the subject, may serve to explain some of these anomalies, and to point out a few facts, which, as far as I have been able to learn, have not been hitherto noticed.

The cotton employed was that used by jewellers, well-carded, perfectly white, and free from imperfections. An analysis of the substance by combustion with oxide of copper in a stream of oxygen yielded the following results :—

$$\begin{array}{lr} \text{Cotton employed} . \quad . \quad . \quad . \quad . & 3.16 \text{ grs.} \\ \text{Carbonic acid produced} . \quad . \quad . & 5.14 \text{ ...} \\ \text{Water produced} . \quad . \quad . \quad . \quad . & 2.06 \text{ ...} \end{array}$$

These proportions are,—

$$\begin{array}{lr} \text{Carbon} . \quad . \quad . & 44.37 \\ \text{Hydrogen} . \quad . & 7.24 \\ \text{Oxygen} . \quad . \quad . & 48.39 \\ \hline & 100.00 \end{array}$$

Lignine calculated from the formula $C_{24} H_{20} O_{20}$:—

$$\begin{array}{lr} \text{Carbon} . \quad . \quad . & 44.44 \\ \text{Hydrogen} . \quad . & 6.17 \\ \text{Oxygen} . \quad . \quad . & 49.39 \\ \hline & 100.00 \end{array}$$

The excess of hydrogen doubtless arises from moisture absorbed by the oxide of copper during the unavoidable delay in mixing it with the cotton.

This cotton, which may be considered as pure lignine, was steeped until thoroughly wetted in a mixture of nitric acid of spec. grav. 1·502, and nearly an equal bulk of strong sulphuric acid, then well-washed with water, and dried at a temperature not exceeding 212°.   In one instance 38·38 grs. of cotton became 66·84 grs., being an increase of 28·46 grs., or 74·15 per cent.   In a second experiment 59·3 grs. of cotton gave an increase of 43·7 grs., or 73·7 per cent.   The gun-cotton, or pyroxyline, thus produced resembled the original cotton in physical properties very closely, and exploded at about 370°, producing no smoke and leaving no residue.

The action of various solvents and reagents upon this substance was found to be as follows :—It is absolutely insoluble in pure water, and nearly so in strong alcohol, æther, whether hydrated or anhydrous, and in a mixture of æther with $\frac{1}{10}$th part of alcohol; but acetic æther instantly destroys its fibre, and dissolves it in large quantity.   The solution yields on spontaneous evaporation a white powder of the same weight as the original pyroxyline, but I have found it very difficult to drive off the last traces of the solvent.   The action of sulphuric acid upon it differs from that exerted upon unaltered cotton; for, while the latter is instantly dissolved by the strong acid, and charred upon a slight elevation of temperature, pyroxyline dissolves with difficulty unless the acid be warmed, evolving at the same time nitric oxide and other gases, and not being charred even upon boiling.   With the aid of heat it dissolves immediately in a solution of potash. By means of these three last-mentioned tests I was able to prove the absence of any unaltered cotton in the product under examination.   The action of other reagents upon gun-cotton was not so decided; it was dissolved, but not without long boiling, by ammonia, the alkaline carbonates, hydrochloric acid, acetic acid, both glacial and dilute, and weak sulphuric acid. These solutions, as well as the two preceding, contained nitric acid; nothing could be precipitated from them by dilution or neutralization; and when evaporated they yielded only a dark brown amorphous matter.   It is evident that none of these reagents restore the lignine in its original condition; and they do not afford any means of ascertaining whether the compound contains the elements of nitric or hyponitric acid.

As there exists a great discrepancy in the accounts given of the increase of weight in making gun-cotton, I examined whether the length of time it was immersed in the acid liquor, or the proportions of the acids employed, were the cause. The length of immersion I found to produce no alteration; but

upon employing two measures of sulphuric acid to one of nitric acid, I obtained a product resembling in all respects ordinary pyroxyline, yet 42·77 grs. gave an increase of only 24·31 grs., or 56·84 per cent. Upon a repetition of this experiment I found the increase to be 59·93 per cent., and again 70·6 per cent. Suspecting from the disparity of these results that something might be dissolved in the acid liquor, I immersed 6·7 grs. of cotton in a large quantity of the mixed acids, but it increased 4·9 grs., or 73·1 per cent. Perceiving that I had obtained an opposite effect to that anticipated, I treated 12·64 grs. of cotton with just sufficient of the mixture to wet it thoroughly: the fibre was evidently somewhat destroyed; the increase in weight was only 6·54 grs., or 51·74 per cent., and the acid liquor squeezed from the cotton, neutralized with ammonia, evaporated to dryness, and heated, gave abundant evidence of organic matter being present. Lest however it might be supposed that the whole had not been converted into pyroxyline, it was treated again with the mixed acids, but that produced an increase of only 0·12 gr. The action of various solvents confirmed its identity with ordinary pyroxyline, while its solubility in potash proved that the transformation had been very nearly complete. A repetition of the experiment gave similar results. It thus appears that the small increase in weight in the preparation of pyroxyline takes place when there is not sufficient nitric acid present to prevent the peculiar action of the sulphuric acid, namely, that of dissolving and altering it. When however the increase amounted to about 74 per cent., I was never able to detect the presence of oxalic acid or other organic matter in the acid liquor; and as no gas is evolved during the preparation of pyroxyline, it may be concluded that there is no secondary product containing carbon.

Subsequently, when Dr. Schönbein had specified *his* method of making gun-cotton, I treated 18·78 grs. of cotton with a mixture of three parts of sulphuric acid and one of nitric acid, sp. gr. 1·5, following his directions. The result was 32·92 grs. of a substance similar to that produced in former experiments, being an increase of 75·20 per cent. On another occasion 80·95 grs. of cotton gave an increase of 61·10 grs., or 75·47 per cent. The action of solvents and reagents confirmed the identity of this pyroxyline with that obtained in my previous experiments, and I was equally able to establish the absence of any secondary product containing carbon.

In determining the ultimate composition of pyroxyline several precautions were found to be necessary. In the ana-

lyses recorded below it was cut into small pieces, and, after the weight was taken, mixed carefully with oxide of copper. To prevent its caking together the admixture of a little asbestos was found useful. This was introduced into a long combustion-tube, then some fresh oxide of copper, and upon it again some fused into lumps so as to fill the whole bore for about 7 inches. Lastly, was added a mixture of copper turnings and reduced copper for about 9 inches. The combustion conducted cautiously in the usual manner gave the following results; the pyroxyline burnt in the sixth experiment having been prepared by Schönbein's method.

	I.	II.	III.	IV.	V.	VI.
Pyroxyline employed	4·09	4·61	3·57	4·85	4·55	2·905
Carbo. acid produced	4·20	4·52	3·42	4·88	...	2·84
Water produced . .	1·19	1·36	...	...	1·34	0·87

Hence in 100 parts,—

	I.	II.	III.	IV.	V.	VI.
Carbon .	27·90	26·74	26·10	27·44	...	26·65
Hydrogen	3·22	3·27	...	...	3·27	3·32

In order to determine the amount of nitrogen the differential mode was adopted, as the method of MM. Will and Varrentrapp is inapplicable to substances containing this element in so highly oxidized a state. The same precautions were taken as in the estimation of carbon; and the collected gases gave the following results after due correction for barometrical pressure :—

	I.	II.	Another specimen.
Carbonic acid .	25·0	38·5	23·9
Nitrogen . . .	5·5	8·5	5·1

These proportions are,—

Nitrogen.		Carbonic acid.
1	:	4·55
1	:	4·53
1	:	4·68

The volumes of the gases represent respectively equivalents of carbon and nitrogen, and since no secondary product is formed in the conversion of lignine into pyroxyline, the 24 equivalents of carbon in the former must be found in the latter. This will give the following ratio in equivalents of carbon and nitrogen according to the three experiments above cited :—

	I.	II.	III.
Carbon	24·0	24·0	24·0
Nitrogen . . .	5·28	5·3	5·12

or 24 : 5, which accords with the proportions assigned by M. Pelouze [*].

The formula which best agrees with these results is the following :—$C_{24} \begin{Bmatrix} H_{15} \\ 5\ NO_4 \end{Bmatrix} O_{20}$, which reckoned to 100 parts, gives—

Carbon	26·23
Hydrogen	2·73
Nitrogen	12·75
Oxygen	58·29

In order to compare pyroxyline with xyloidine, I treated starch with fuming nitric acid until the whole was converted into a gelatinous mass. The addition of water then threw down a white powder, which was subsequently well-washed and dried. The iodine test proved the absence of all unaltered starch. The xyloidine thus obtained explodes at about 360°, leaving a carbonaceous residue. It is slightly soluble in æther, with which it is capable of forming a peculiar compound not yet investigated ; more so in alcohol, but most of all in æther mixed with a small proportion of alcohol, or in acetic æther. It is dissolved by strong sulphuric acid without the aid of heat, and by boiling solutions of potash, ammonia, hydrochloric acid and dilute sulphuric acid. These solutions contain nitric acid, and nothing is precipitated from them by dilution or neutralization. Xyloidine is also soluble in strong acetic acid, or in nitric acid, whether fuming or of sp. gr. 1·25, but is reprecipitated from either by dilution.

It was also found that nitric acid of ordinary strength (sp. gr. 1·45) answered equally well in the preparation of this substance ; but when acid of sp. gr. 1·41 was employed no such result was obtained. Starch treated with a mixture of equal measures of nitric and sulphuric acids produced a substance of greater combustibility, and more closely resembling pyroxyline, but differing from it in being soluble in glacial acetic acid, and in a mixture of æther with one-tenth part of alcohol, as also in the action that acetic æther exerts upon it. Xyloidine also when subjected to the mixed acids gave a product identical with the above, as far at least as the action of solvents can prove.

Xyloidine burnt by means of oxide of copper, with the usual precautions, gave the following results. The substance employed in the third experiment was made from arrow-root.

	I.	II.	III.
Xyloidine employed . .	4·77	5·23	6·75
Carbonic acid produced .	5·30	5·91	7·87
Water produced . . .	1·84	1·96	2·80

Hence in 100 parts,—

	I.	II.	III.
Carbon . .	30·30	30·82	31·79
Hydrogen .	4·28	4·16	4·60

In the determination of nitrogen by the differential method the proportions of the gases obtained were,—

	I.	II.	III.
Carbonic acid .	70·7	53·4	53·8
Nitrogen . . .	10·6	6·9	8·0

These are in the proportion of—

	I.	II.	III.
Carbon . .	24·0	24·0	24·0
Nitrogen . .	3·59	3·10	3·57

These numbers suggest the simple substitution product $C_{24}\begin{Bmatrix} H_{17} \\ 3NO_4 \end{Bmatrix} O_{20}$, in which the per-centage of carbon would be 31·37, and of hydrogen 3·70; yet the amount of nitrogen is somewhat too great, and there is far from being sufficient evidence to prove the definiteness of the substance itself. The wide difference also in the results obtained by various chemists can scarcely be accounted for, except upon the supposition that they have operated upon very different substances.

The solubility of xyloidine in nitric acid led me to examine whether any alteration could be effected upon pyroyxline by similar means. The most dilute acid which I found to have any effect upon it in the cold was that of sp. gr. 1·414; but the alteration took place by means of this only after long standing, and but to a slight extent. Nitric acid of sp. gr. 1·45 however is capable of dissolving pyroxyline, and alters both its composition and properties, as will be presently described; whilst fuming nitric acid has not the slightest effect upon it. The new product just mentioned is acted upon somewhat differently by various solvents, according to whether it exists in a fibrous condition, or in powder as precipitated from solution; yet I have found by experiment that no alteration in weight is effected by this change of condition. When in fibre it is slightly soluble in strong alcohol, æther, a mixture of æther with one-tenth part of alcohol, and acetic æther; but when in the pulverulent state it is very soluble in these menstrua, and in glacial acetic acid. In either con-

dition it leaves a carbonaceous residue on combustion, is dissolved by nitric acid, whether of sp. gr. 1·25 or 1·5, and reprecipitated upon dilution. Strong sulphuric acid also dissolves it in the cold, and chars it at a temperature below 180°. These two last properties show that the original pyroxyline was perfectly free from admixture with this new substance.

There occurs a considerable decrease of weight through this transformation. In the first experiment 32 grs. of substance operated upon gave 25·82 grs. of the new product; in the second 43·64 grs. of the one yielded 34·68 of the other. Now assuming the increase in the preparation of pyroxyline to be 75 per cent., the weight of the new product above that of the original cotton would be, as calculated from these figures, 41·1 and 39·05 per cent.

When this new product, whether in the fibrous or the pulverulent condition, was treated with a mixture of equal parts of nitric and sulphuric acids, it increased considerably in weight, and the resulting substance had all the properties of pyroxyline as prepared in the usual manner. 11·16 grs. of the one yielded 13·56 grs. of the other; the quantity that should theoretically have been obtained, calculating it from the decrease in making the new product, is 13·84 or 14·04 grs. Again, 12·35 grs. of the substance as precipitated from solution gave 15·75 grs., the theoretical amount would have been 15·31 or 15·54 grs. This result proves the distinctness of the new product from xyloidine, a fact that could not have been ascertained from the action of the before-mentioned solvents.

Whilst engaged in obtaining these results, I also examined the action of nitric acid of various degrees of strength upon pure cotton. By treating it with nitric acid of sp. gr. 1·5 I obtained a product evidently different from gun-cotton, but as it did not appear to be homogeneous throughout, I passed on to investigate the action of a weaker acid. That of sp. gr. 1·45 gave a substance which proved to be identical with the product of the action of the same acid upon pyroxyline. Upon a repetition of the experiment 68·54 grs. increased in weight 14·61 grs., or 21·31 per cent.—a smaller increase than might have been anticipated, but which may easily be accounted for by the fact that the whole cotton had not been transformed, as was proved by a considerable portion being left undissolved by a boiling solution of potash. Nitric acid of sp. gr. 1·414 produced the same alteration, but only to a small extent, and after long standing. 23·75 grs. of cotton soaked in nitric acid of sp. gr. 1·516 became a hard mass,

and increased in weight 13·49 grs., or 56·8 per cent.; the action of various solvents upon the resulting substance indicated that it was a mixture of pyroxyline and the new product. On another occasion, when the transformation by means of nitric acid sp. gr. 1·47 proved to be complete, 29·52 grs. of cotton increased 9·51 grs., or 32·89 per cent. But in order to obtain a substance sufficiently pure for analysis 16·29 grs. of cotton were treated with enough nitric acid to dissolve the whole; the new product was precipitated by dilution, and the increase in weight was found to be 5·34 grs., or 32·78 per cent. In these instances there occurred a secondary product containing carbon not precipitable by water.

When this was subjected to combustion with oxide of copper, the following results were obtained:—

	I.	II.	Another specimen.
Substance employed .	3·15	2·985	3·165
Carbonic acid produced	3·58	3·39	3·55
Water produced . .	1·00	1·01	1·14

Hence in 100 parts,—

Carbon .	30·99	30·97	30·59
Hydrogen	3·52	3·75	4·00

I was unable to obtain any very accurate estimation of nitrogen by the differential method: the results most to be depended upon were—

Carbonic acid . .	120·7	76·7
Nitrogen	13·6	8·3

In the proportion of

Carbon . . .	24·0	24·0
Nitrogen . . .	2·7	2·6

These numbers lead me to think that there are 3 equivalents of nitrogen in the compound, especially as I observed during the combustion that the substance became charred even 1 or 2 inches beyond the glowing charcoal, which will account for the deficiency of nitrogen when compared with the carbonic acid. Hence the composition of the new product coincides very nearly with that calculated from the formula $C_{24} \left\{ {H_{17} \atop 3\,NO_4} \right\} O_{20}$, namely,

Carbon	31·37
Hydrogen . . .	3·70
Nitrogen	9·15
Oxygen	55·78
	100·00

Under this supposition the increase in weight in the preparation would be 41·66 per cent. ; very similar to that calculated from the results obtained by the action of nitric acid, sp. gr. 1·45, on pyroxyline, namely, 39·05 and 41·1 per cent.

In order to add an additional proof of the identity of the two substances obtained by the action of nitric acid of sp. gr. 1·45 on cotton and on pyroxyline, and also of the fact that pyroxyline is reproduced by the action of mixed sulphuric and nitric acids upon the new product, the experiment was repeated with a portion of the substance made from pure cotton : the result was pyroxyline. In the transformation 26·56 grs. became 38·04 : now these 26·56 grs. were produced from 21·81 grs. of the original cotton ; hence the increase upon the cotton itself would be 16·23 grs., or 74·4 per cent., coinciding with the amount usually obtained in the preparation of pyroxyline.

I. From these results it appears that in the treatment of woody fibre by nitric acid raised to its highest degree of strength by the addition of sulphuric acid, 5 equivalents of the acid combine with 1 of lignine to produce pyroxyline, displacing 5 equivalents of the elements of water, as indicated by the formula $C_{24} \left\{ \begin{matrix} H_{15} \\ 5\,NO_4 \end{matrix} \right\} O_{20}$. The amount per cent. of carbon and hydrogen hence deduced closely agrees also with that assigned by Mr. Ransome [*] and M. Pettenkofer [†].

		Calculated.	Ransome.	Pettenkofer.
Carbon	.	26·23	26·28	26·26
Hydrogen	.	2·73	3·16	2·75

In this case the synthetical experiment would give an increase of 69·44 per cent.—nearly the amount obtained in the best experiments. My own analyses however have yielded a somewhat larger amount of carbon.
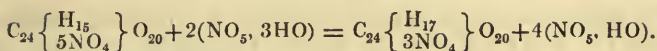
II. If lignine be treated with nitric acid combined with more than 1 equivalent of water, another compound is produced, containing a smaller proportion of the elements of nitric acid, most probably $C_{24} \left\{ \begin{matrix} H_{17} \\ 3\,NO_4 \end{matrix} \right\} O_{20}$, and very closely resembling, but not identical with, pyroxyline.

$$C_{24} H_{20} O_{20} + 3(NO_5, 2HO) = C_{24} \left\{ \begin{matrix} H_{17} \\ 3\,NO_4 \end{matrix} \right\} O_{20} + 9HO.$$
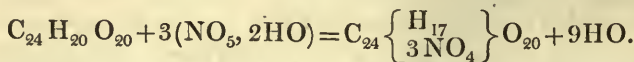
Also if pyroxyline itself be treated with nitric acid containing 3 equivalents of water, the same compound results :

[*] Phil. Mag., January 1847.
[†] *Pharmaceutisches Central Blatt*, Dec. 30th, 1846.

$$C_{24} \left\{ \begin{matrix} H_{15} \\ 5NO_4 \end{matrix} \right\} O_{20} + 2(NO_5, 3HO) = C_{24} \left\{ \begin{matrix} H_{17} \\ 3NO_4 \end{matrix} \right\} O_{20} + 4(NO_5, HO).$$

And this transformation may be reversed.

Whilst completing my examination of this substance, my attention was drawn to the communication of M. Payen in the *Comptes Rendus* of Jan. 25th, where some properties of " coton hypoazotique " are described. It is possibly the same; yet, in order to express its distinctness from pyroxyline, I would propose as the appellation of my substance cotton-xyloidine.

Before concluding I would acknowledge my obligations to several chemists whose published investigations on the same subject have suggested many of my experiments, and more particularly to Professor Fownes for the valuable advice with which from time to time he has favoured me.

CCII. *On the Action of Nitric Acid on Cymol. First Part.* By H. M. Noad, *Esq.*

Formation of Toluylic and Nitrotoluylic Acids.

WE possess in benzoic acid and its derivatives a well-defined group of substances connected in a variety of ways with a large number of organic families. These interesting bodies have been made subjects of investigation by several chemists. The study has been a fascinating one, and has resulted in a thorough development of their history, and of the products of their decomposition.

This group may be considered the prototype, as it were, of several parallel groups, presenting a very close relation with the composition of the benzoyl family. The careful study of the former has gradually made these known to us, in the same manner as the study of alcohol and its derivatives made us acquainted with several corresponding classes of bodies.

The methyl compounds, with which we have become familiar through the experiments of Dumas and Peligot[*] on pyroxylic spirit, and the amyl series, the origin of which we owe to the investigations of Cahours[†] on fusel oil, form two groups, the analogy of which with the alcohol series can be traced in every direction; they differ in composition from the former only by a multiple of $C_2 H_2$, thus—

$$HO, C_2 \ H_3 \ O = \text{hydrated oxide of methyl.}$$
$$HO, C_4 \ H_5 \ O = \text{hydrated oxide of ethyl.}$$
$$HO, C_{10} H_{11} O = \text{hydrated oxide of amyl.}$$

[*] Liebig's *Annalen*, xv. 1.   [†] Ibid. xxx. 288.

The same relation is likewise observed in the acids resulting from the oxidation of these bodies, and these acids are perhaps even better adapted to point out this interesting regularity, as the gaps existing between the different alcohols are filled up in the series of the acids, which may be formed in a great variety of ways. A glance at the following table will render the regularity above alluded to at once obvious:—

Alcohols.	Acids.
$HO, C_2 H_3 O$, pyroxylic spirit.	$HO, C_2 HO_3$, formic acid.
$HO, C_4 H_5 O$, alcohol.	$HO, C_4 H_3 O_3$, acetic acid.
	$HO, C_6 H_5 O_3$, metacetonic acid.
	$HO, C_8 H_7 O_3$, butyric acid.
$HO, C_{10} H_{11} O$, fusel oil.	$HO, C_{10} H_9 O_3$, valerianic acid.
	$HO, C_{12} H_{11} O_3$, caproic acid.
	$HO, C_{14} H_{13} O_3$, œnanthylic acid.
	$HO, C_{16} H_{15} O_3$, caprylic acid.
	$HO, C_{18} H_{17} O_3$, pelargonic acid.
	$HO, C_{20} H_{19} O_3$, capric acid.
&c.	&c.

Now it seems that benzoic acid is a member of a similar series of acids, distinguished from each other by the same amounts of carbon and hydrogen, and that we may expect to find a representative of every single term of the benzoyl series in these other families. An examination of cumin oil by MM. Gerhardt and Cahours[*] has brought to light a new acid,—cuminic acid, $HO, C_{20} H_{11} O_3$, which exhibits a perfect analogy with benzoic acid, not only in its physical properties, but also in the metamorphoses which it undergoes when acted on by chemical agents. This acid is distinguished from benzoic, $HO, C_{14} H_5 O_3$, by containing $3(C_2 H_2)$ more; it stands to benzoic acid as valerianic acid stands to acetic acid, and when distilled with lime it is converted into cumol, $C_{18} H_{12}$, which represents benzol, $C_{12} H_6$, in the benzoyle series. The same investigation of cumin oil has made us acquainted with another carbo-hydrogen cymol, $C_{20} H_{14}$, which is also a representative of benzol in another series; but up to the present time the acid from which this carbo-hydrogen derives, and which would contain $4(C_2 H_2)$ more than benzoic acid, has not been discovered.

By the investigations of Pelletier and Walter[†] on the products of the distillation of resinous substances, of Deville[‡] on the distillation of tolu balsam, and of Boudault and Glenard[§] on the dry distillation of the dragon's blood, an addi-

* Liebig's *Annalen*, xxxviii. 67.
† Ibid, xxviii. 295.
‡ *Ann. de Chim. et Phys.* 3 sér. t. iii. p. 168.
§ *Journ. de Pharm. et de Chim.* 3 sér. t. vi. p. 250.

These per-centages, translated into the most simple expression, lead to the formula, $C_{81} H_{11} NO_6$ as may be seen from the following table :—

		Theory.		Experiment. Mean.
Carbon . . . 18	108	59·668	59·41
Hydrogen . . 11	11	6·077	6·29
Nitrogen . . 1	14	7·735	7·66
Oxygen . . . 6	48	26·520	
	181	100·000	

Careful and repeated examinations for sulphur proved the absence of this element as a component of the new white substance. I have been unable to produce a compound to control the proposed formula, though several methods were adopted; amongst others, I attempted to form a lead compound by adding acetate of lead to an ammoniacal solution of the substance; I obtained merely a bulky precipitate, consisting of little else than oxide of lead.

This substance is sparingly soluble in cold water, much more so in boiling water; insoluble in alcohol and æther; soluble in hydrochloric acid, which appears to be driven off by evaporation, leaving the substance in large crystals. In a large quantity of nitric acid it dissolves with a slight evolution of gas; the solution evaporated spontaneously furnishes long crystals, which are in all probability a new acid; if dissolved in a small quantity of nitric acid, the mixture becomes spontaneously heated, violent action takes place, and the product is lost; frequently the substance becomes blackened into charred masses. It is soluble in ammonia, from which it is again recovered by the evaporation of the ammonia. It is soluble in the fixed alkalies, and is precipitated from these solutions by saturating with an acid.

In a short paper, entitled "Valerianic Acid and a new body from Casein," Baron Liebig[*] describes a new substance obtained by fusing casein with hydrate of potash until an evolution of hydrogen takes place along with ammonia. On saturating with acetic acid the aqueous solution of the fused mass an aggregate of fine needles was produced, which were purified by repeated solution in carbonate of potash and re-precipitation by acetic acid. A preliminary analysis led to the formula $C_{16} H_9 NO_5$, differing from the result I obtained in the analysis of the white substance from cochineal by two carbon, two hydrogen, and one oxygen. The properties of the two bodies being however so analogous, it is extremely probable that they are identical, a presumption I am sup-

* Liebig's *Annalen,* vol. lvii. p. 127.

ported in by a comparison of a specimen kindly furnished me by Dr. Hofmann *; further investigations will clear up this point: in the meantime I refrain from proposing a name, as Liebig † has lately proposed the name Tyrosine for the substance prepared from casein. As the latter body arises evidently from a process of oxidation, and as I had obtained the first crop of crystals from a liquid from which the colouring matter had been precipitated by the basic nitrate of lead, I thought that this body might owe its formation to the action of the nitric acid liberated by the sulphuretted hydrogen; but this supposition proved to be erroneous, for in later experiments in which acetate of lead had been used, the same body, and in exactly the same quantity, was obtained. From this we may assume that this substance is contained ready-formed in the cochineal insect.

My engagements for the present preventing me from continuing these researches, I must defer for a future period their completion, but hope to be enabled to communicate to the Society a second paper. In conclusion I may be allowed to express my thanks to my friend Dr. Hofmann for his valuable instruction in the methods of organic research, and his kind advice during the progress of this investigation.

CCVI. *On the Nitrates of Bismuth and Copper.* By Mr. John Hall Gladstone, *of University College.*

IN the *Annales de Chimie* for October 1846 appeared a paper by M. Gerhardt, in which he shows that the subnitrate of copper, in whatever manner prepared, has the composition $NO_5, 4CuO, 3HO$; and that the pale blue crystals of neutral nitrate contain four atoms of water of crystallization instead of three, as had been formerly believed.

Upon the publication of this Professor Graham drew my attention to the subnitrate of bismuth, and expressed his opinion that there might be a similar error in the formula assigned to it; especially when it was considered that the per-centage of oxide of bismuth would be almost the same in either case. Now M. Duflos had long since ascribed to the subnitrate of bismuth, formed by decomposing the nitrate by twenty-four times its weight of water, the formula $4BiO, NO_5 + 3HO$, thus coinciding with that of the copper salt as determined by M. Gerhardt. It became desirable therefore that the subnitrate of bismuth formed by heating the neutral

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* This specimen had been prepared by Baron Liebig himself.—A. W. H.
† Researches on the Chemistry of Food, p. 16.

nitrate, as well as the neutral nitrate itself, should be re-examined.

The subnitrate under consideration may be easily prepared in a state of purity by dissolving metallic bismuth in strong nitric acid, from which the neutral nitrate crystallizes spontaneously, and by subjecting these crystals to a heat of about 300° F. for some hours. The subnitrate thus produced is a white powder yielding up its acid and water at about 500°.

In order to determine the amount of water, a weighed portion of the salt was heated to redness in a tube of hard glass, and the resulting gases passed over metallic copper for the purpose of decomposing the nitric acid, and the water was collected by a chloride of calcium tube. In the first experiment oxide of lead kept at about 300° F. was employed instead of copper, and was found to retain the whole of the nitric acid.

	I.	II.	III.	Fresh prep.
Substance employed	18·21	22·00	13·14	23·17
Water produced .	0·57	0·79	0·43	0·69

These numbers give respectively 3·1, 3·6, 3·2 and 3·0 per cent.

An estimation of the nitrogen by the absolute method yielded from 17·82 grs. of substance 2·85 cubic inches of gas, equivalent, after due correction, to 18·49 per cent. of nitric acid.

An estimation of the oxide of bismuth, by simply heating the substance to redness in a platinum crucible, gave from 33·635 grs. of subnitrate 26·65 grs. of metallic oxide, or 79·23 per cent.

These numbers very nearly coincide with those deduced from the formula of Prof. Graham, $HO, NO_5 + 3BiO$.

	By experiment.	By calculation.
Oxide of bismuth . .	79·23	79·01
Nitric acid	18·49	17·99
Water (aver. of 4 expts.)	3·22	3·00
or Nitrogen	4·81	4·66

There is more than one subnitrate produced by the action of water, and in all probability the "magistery of bismuth" of pharmacy is a mixture of two or more of these. A single experiment of mine yielded 0·9 per cent. of water.

The analysis of the neutral nitrate is attended with far greater difficulty, since it is impossible to free the substance entirely from adhering acid and water without running considerable risk of efflorescence or decomposition. For the first determination of the amount of water, the crystals were drained, dried between folds of blotting-paper, pounded, left

for a day or two *in vacuo* with sticks of caustic potash, and rubbed in dry calico ; for the second, the crystals were merely crushed, and pressed for a few minutes between folds of paper ; while for the third they were dried, but not pounded.

The following were the results obtained :—

	I.	II.	III.
Substance employed	19·02	16·46	15·63
Water produced . .	3·715	3·21	3·04

These numbers give respectively 19·5, 19·5 and 19·4 per cent. of water ; a close agreement, when it is considered that the substance employed in the third experiment might not be free from adhering water—a circumstance almost impossible in the first.

A similar uniformity exists in the per-centage of oxide of bismuth obtained in different manners.   In the first experiment the crystals were pounded, and pressed for a few minutes between folds of blotting-paper, subsequently heated at 300°, so as to obtain the subnitrate already analysed, and, lastly, all the acid and water expelled by a higher degree of temperature.   For the second experiment a fresh preparation of the nitrate was made, and the pounded salt was dried *in vacuo* with sticks of caustic potash.   In the third and fourth crystals were employed which had remained three days in paper : efflorescence was just beginning to appear.   In the fifth experiment the best-looking crystals were chosen, and the oxide of bismuth determined by precipitation.   Hoping to obtain the nitrate of bismuth from a less acid solution, I dissolved some of the salt in very dilute nitric acid, but no crystals could be obtained until the evaporation had been carried almost to dryness, when of course the acid liquor had become very concentrated ; the salt however was pounded and dried, and furnished the sixth experiment.   For the seventh some metallic bismuth was allowed to remain in nitric acid until the acid was so far exhausted as to have little action upon the metal : the mother-liquor was presently filled with minute crystals, which were dried and subjected to analysis. The following are the results of these several experiments :—

	I.	II.	III.	IV.	V.	VI.	VII.
Subs. used .	29·19	27·01	26·27	22·02	19·95	14·33	14·89
Subnit. prod.	17·84	...	16·00	13·69			
BiO obtained	13·98	12·98	12·72	10·69	9·54	6·92	7·15

These numbers give respectively 47·89, 48·05, 48·42, 48·54, 47·82, 48·29 and 48·02 per cent. of oxide of bismuth. And if we consider the atomic weight of the subnitrate as $\dfrac{300\cdot21}{3}$, *i. e.*

100·07, the weight of a single atom of neutral nitrate calculated from the first, third and fourth experiments, will be 163·7, 164·1 and 161·0.

These results are intermediate between the numbers calculated from the formulæ

	$BiO, NO_5 + 3HO.$	$BiO, NO_5 + 4HO.$
Oxide of bismuth	49·39	46·76
Nitric acid . .	33·74	31·95
Water	16·87	21·29
	100·00	100·00
Weight of atom .	160·07	169·07

They approximate most closely to the numbers deduced from the formula $2(BiO, NO_5) + 7HO.$

	Average of experiments.	$2(BiO, NO_5) + 7HO.$
Oxide of bismuth .	48·15	48·05
Nitric acid . . .	32·38	32·81
Water	19·47	19·14
	100·00	100·00

If we employ the equivalent for bismuth adopted by Berzelius and Regnault, the neutral nitrate becomes $Bi_2O_3, 3NO_5$, which would be combined with $10\frac{1}{2}$ equivalents of water. If the, not unusual, proportion of 10 atoms be assigned to it, the salt will be expressed by the formula $Bi_2O_3, 3NO_5 + 10HO.$

This last view does not correspond so closely as the former with the experimental results, but is not altogether incompatible with them.

	Average of experiments.	$Bi_2O_3, 3NO_5 + 10HO.$
Oxide of bismuth .	48·15	48·49
Nitric acid . . .	32·38	33·11
Water	19·47	18·40
	100·00	100·00

By adopting the high equivalent for bismuth the subnitrate before analysed would be represented by $HO, NO_5 + Bi_2O_3.$

I have entered minutely into the detail of my experiments upon nitrate of bismuth, because M. Heintz has recently given * his concurrence to the formula $3NO_5 + Bi_2O_3 + 9HO$; or, if we express the same in the terms of the other theory, $BiO, NO_5 + 3HO$: he however found somewhat more than the calculated amount of water, a circumstance he attributes to moisture still adhering to the nitrate itself; yet seeing the salt is efflorescent, I cannot but think that the difficulty of drying it is overrated. M. Freundt † gives the following

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* *Annuaire de Chimie,* 1846, Millon et Reiset.
† Chemical Gazette, March 1st, 1844.

as the results of his analyses of nitrate of bismuth prepared in three different manners :—

Oxide of bismuth	49·00	49·00	48·30
Nitric acid . .	33·25	32·33	31·08
Water	17·75	...	20·62
	100·00		100·00

These numbers, though they do not coincide well with those deducible from any formula, rather favour my view of the composition of this salt. One principal object of M. Freundt's paper is to show that when crystals of nitrate of bismuth are thrown into pure water, besides the subnitrate precipitate we have some of the original salt kept in solution by the liberated acid. I repeated his experiments, and after separating a sub-nitrate which crystallized from the filtered solution in beautiful feathers of a silvery lustre as soon as it began to evaporate, I obtained crystals having the usual appearance of nitrate of bismuth: 14·93 grs. yielded 7·10 grs. of oxide, which is equivalent to 47·55 per cent.; thus confirming at once M. Freundt's statement and my former analyses.

It was interesting to observe whether the nitrate of bismuth was thus separated entirely from nitrate of copper in the proportion of water these salts contain, and the nature of their constitution.

Nitrates of Copper.

Upon crystallizing a solution of nitrate of copper at about 60° F. (20° Cent.), I uniformly obtained fine blue prismatic crystals, apparently unmixed with any of the salt, containing 6 atoms of water; a result which may be attributed to my having operated at so high a temperature.

The crystals thus obtained are decidedly deliquescent, and do not effloresce like those analysed by M. Gerhardt, which appear to have contained a portion of the higher hydrate. Hence it is impossible to free this salt absolutely from water by means of blotting-paper, but when placed *in vacuo* the crystals speedily become very brittle, and assume a lustrous appearance. The amount of metallic oxide and water was determined as in the analysis of the bismuth salts, and yielded the following results :—

	Dried in paper.			Dried *in vacuo*.		
	I.	II.	III.	IV.	V.	VI.
Substance used	36·51	19·49	7·81	22·02	12·92	9·79
CuO obtained .	12·02	6·31	2·53	7·31	4·32	3·24

These numbers are equivalent to 32·92, 32·38, 32·4, 32·4, 33·44 and 33·1 per cent. of oxide of copper: mean, 32·77.

	Dried in paper.		Dried *in vacuo*.	
	I.	II.	III.	IV.
Substance employed	14·70	11·75	9·58	10·04
Water obtained . .	3·56	2·70	2·07	2·11

These numbers are equivalent to 24·2, 22·9, 21·6 and 21·1 per cent. of water: mean 22·45; a result which agrees closely with the numbers calculated from the formula originally assigned to this salt by Professor Graham.

	Average of experiments.	$CuO, NO_5 + 3HO.$
Oxide of copper .	32·77	32·90
Nitric acid . . .	44·78	44·73
Water	22·45	22·37
	100·00	100·00

The analysis of the other hydrate of nitrate of copper made by Mr. Graham, indicating 6 atoms of water, is admitted as correct by M. Gerhardt.

The subnitrate produced by heating the neutral nitrate of copper was also analysed in a similar manner; and the following are the results:—

Substance employed . . . 15·75 grs.
Oxide of copper obtained . 10·39 ...

Equivalent to 66·0 per cent. of oxide of copper.

Substance employed . 6·81 grs.
Water produced . . 0·76 ...

This is equivalent to 1·11 per cent. of water; a result which confirms the view taken by M. Gerhardt of the composition of this salt, as will be perceived by the annexed numbers:—

	By experiment.	$NO_5, 3HO, 4CuO.$
Oxide of copper .	66·0	66·23
Nitric acid . . .	22·9	22·51
Water	11·1	11·26
	100·0	100·00

Hence it is evident that the true composition of the prismatic crystals of nitrate of copper being $CuO, NO_5 + 3HO$, while that of nitrate of bismuth is $2(BiO, NO_5) + 7HO$, there is no relation between the two salts: and the subnitrates of these metals produced by heating their nitrates being respectively $4CuO, NO_5, 3HO$, and $3BiO, NO_5, HO$, shows that they are also entirely separated in this respect.

The rational formulæ for these two classes of salts to which I am disposed to give a preference, are as follows :—

I. Crystallized nitrate of bismuth   . $2(BiO, NO_5) + 7HO$
   Subnitrate of bismuth .   .   .   . $HO, NO_5 + 3BiO$.

II. Rhomboidal nitrate of copper $CuO, NO_5 + 6HO$.
    Prismatic nitrate of copper . $CuO, NO_5 + 3HO$.
    Subnitrate of copper . . . $CuO, NO_5 + 3(CuO, HO)$.

The subnitrate thus appears to be formed by replacing the 3 atoms of water in the prismatic nitrate by 3 atoms of the hydrated oxide of copper.

CCVII. *On Crystallography, with a Description of a New Goniometer and Crystallonome.* By H. B. Leeson, *M.D.**

DISCRIMINATIVE chemical researches have not received that assistance from crystallography which might have been reasonably anticipated from the natural distinction of form peculiar to various substances whose atoms are free to assume that symmetrical arrangement which is the natural result of certain attractive and repulsive forces pertaining to them.

Many difficulties have concurred to deter persons from devoting greater attention to this branch of science, and to induce a belief that the advantages to be obtained therefrom are not sufficient to compensate the requisite amount of study and labour.

Greater facility in the practical determination of crystalline forms will, it is believed, result from the use of the instruments herewith submitted to the Society ; and it is also hoped that the principles of classification now proposed will obviate many of those difficulties consequent on the want of uniform and simple rules whereby to refer a given crystal to its appropriate class and order.

The introduction of any other system, founded on the three gubernatorial axes of Weiss, might perhaps be deemed superfluous, were it not that neither Weiss himself, nor they who have succeeded him, appear to have realized that simplicity or perfection of which the fundamental principle seems to be susceptible.

By referring to the comparative tables of the systems of different authors accompanying the present paper, it will be apparent, not only that the methods of classification are in many instances imperfect and obscure, but also that the

XIX. *Artificial formation of Urea from Fulminic Acid.* By J. H. GLADSTONE, PH. D.

During the investigations of Professor Liebig upon fulminic acid, he was led to believe, that urea was formed when the fulminate of copper and ammonia was decomposed by sulphuretted hydrogen. A statement to that effect is to be found in the "Lancet" of Dec. 7th, 1844; but the fact was never established by satisfactory experiment. The discovery of Wöhler, that urea may be artificially produced from cyanic acid and ammonia, rendered this transformation of fulminic acid antecedently probable, upon the supposition of the isomerism of the two acids: since, however, this has been disputed, it became desirable to resume an inquiry so interesting and important in a theoretical point of view.

Fulminating silver was prepared in the manner recommended by Geiger; *i. e.* one part of metallic silver was dissolved in 10 parts of nitric acid, sp. gr. 1·36, and the solution was poured into 20 parts of alcohol, sp. gr. 0·85. The mixture was heated until nitrous ether was formed with considerable ebullition, and then, the heat being removed, was allowed to remain till the solution became troubled, and fulminating silver was deposited in crystals. The salt thus prepared was well washed by decantation, and set aside in a warm place with metallic copper, in vessels containing a large amount of water. By this means the silver was wholly precipitated, while copper entered into combination with the fulminic acid, forming a salt, which remained in solution. The liquid was then poured off, and treated with a large excess of ammonia, by which one of the atoms of metal in the fulminate of copper was displaced, and ammonia substituted. Through this solution of fulminate of copper and ammonia, sulphuretted hydrogen was passed, until it ceased to produce a precipitate. The sulphuret of copper was separated by filtration, and the solution that resulted, containing sulphuret of ammonium, free ammonia, and the products of decomposition, was evaporated. During this process, a little sulphuret of copper and suboxide of copper separated, and afterwards a greyish powder, which, when decomposed by acid, yielded suboxide of copper, and an acid soluble in water, giving with a persalt of iron, the deep red tint, characteristic of sulphocyanogen. The

solution filtered from this precipitate, and concentrated to a small bulk, gave crystalline precipitates with oxalic and nitric acids, closely resembling the salts which these acids produce with urea : in addition to this, a substance in combination with ammonia was obtained, which also gave the red colour peculiar to sulphocyanogen by the iron test.

In order to separate these two bodies completely, the following method was found efficacious. The solution was warmed with a quantity of hydrated oxide of lead, until all the ammonia was expelled: by this means the whole sulphocyanogen was precipitated as basic sulphocyanide of lead, and was separated by filtration. The resulting liquid still contained a trace of copper, which was removed by a little sulphuretted hydrogen, and the now colourless solution yielded, upon evaporation, crystals of apparently pure urea.

Analysis of the urea.—The urea was converted into oxalate, and burnt in the usual manner with chromate of lead. The following are the results of the analysis :

I. 0·4165 grm. of salt yielded 0·357 grm. carbonic acid, and 0·1825 grm. water.

II. 0·3345 grm. of salt purified by re-crystallization from water, yielded 0·2815 carbonic acid, and 0·146 water.

These numbers reckoned to 100 parts, and compared with those calculated from the formula of oxalate of urea $C_2 H_4 N_2 O_2, C_2 O_3 + HO$, afford :

	Calculated.	Found by experiment.	
		I.	II.
Carbon	22·86	23·38	22·93
Hydrogen	4·76	4·88	4·84
Nitrogen	26·67	—	—
Oxygen	45·71	—	—
	100·00		

An analysis of the nitrogen was also made by the differential method. Six tubes of mixed gases were collected, of which the 3rd, 4th, and 5th contained the following proportions :

Carbonic acid	202	188	129
Nitrogen	98	94	67

These numbers are very nearly as 2 : 1 ; the proportion in which the carbon and nitrogen exist in oxalate of urea.

Analysis of the sulphocyanide.—The mixture of oxide of lead and lead-salt, which was separated from the solution containing the urea, was

decomposed by means of sulphuret of ammonium; the sulphuret of lead was removed by filtration; the solution, after being boiled to expel an excess of the reagent, was rendered acid with nitric acid, and nitrate of silver was added. This produced a copious white curdy precipitate, very susceptible of decomposition by light. The copper-salt, which separated during the first evaporation, was treated in a similar manner.

A weighed portion of the silver-salt was oxidized by means of strong nitric acid, and, when completely dissolved, the silver was precipitated by hydrochloric acid, and the sulphuric acid, afterwards, by chloride of barium. In this experiment 0·465 grm. of salt yielded 0·400 grm. of chloride of silver, and 0·6565 grm. of sulphate of barytes.

Another portion, weighing 0·573 grm. of the salt, purified by re-crystallization from ammonia, was burnt with chromate of lead, and yielded 0·1435 grm. of carbonic acid.

These numbers reckoned to 100 parts, and compared with those calculated from the formula of sulphocyanide of silver, $Ag, C_2 NS_2$, the nitrogen being estimated by the loss, afford:

	Calculated.	Found by experiment.
Silver	65·06	64·80
Carbon	7·23	6·83
Nitrogen	8·43	8·90
Sulphur	19·23	19·47
	100·00	100·00

It thus appears that urea and sulphocyanide of ammonium are the products of the decomposition of fulminate of copper and ammonia by sulphuretted hydrogen; and during the several repetitions of the experiment I observed no other product.

Upon the long-received view of the constitution of fulminic acid, the decomposition is easily explained. When the copper-salt is decomposed, the one atom of acid, previously in combination with the metallic oxide, unites with two of sulphuretted hydrogen;

$$Cy\,O \,\&\, 2\,HS \,=\, Cy\,S_2 \,\&\, HO \,\&\, H,$$
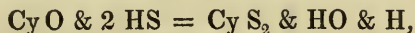
while the other atom of acid, that existed in combination with ammonia in the double salt, resolves itself into urea:
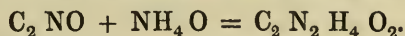
$$C_2\,NO \,+\, NH_4\,O \,=\, C_2\,N_2\,H_4\,O_2.$$

The whole decomposition may be thus expressed. One atom of fulminate of copper and ammonia, with three atoms of sulphuretted

hydrogen, that is, $Cu\,O$, $NH_4\,O$, $C_4\,N_2\,O_2$ & $3\,HS$, are resolved into

1 at. of Sulphuret of copper	.	. .	$Cu\,S$
1 „ Urea	. . . .	. . .	$C_2\,N_2\,H_4\,O_2$
1 „ Sulphocyanogen *ic acid*	.	. .	$S_2\,C_2\,N$
2 „ Water	. . . .	. . .	$H_2\,O_2$
1 „ Hydrogen	. . . . . .	. . .	H

$$\overline{\qquad Cu\,S_3\,C_4\,N_3\,H_7\,O_4 \qquad}$$
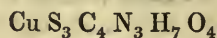
It is probably owing to this atom of hydrogen, eliminated during the formation of sulphocyanogen, that I always found a considerable quantity of the oxide of copper reduced to the state of suboxide.

ON

THE GROWTH OF PLANTS

IN VARIOUS GASES.

BY

Dr. J. H. GLADSTONE and G. GLADSTONE, Esq.*

THAT both plants and animals are very dependent upon the chemical composition of the atmosphere in which they live, and that the constituents of it play important functions in their œconomy, are matters of every-day observation. These constituents are oxygen, nitrogen, aqueous vapour, a small amount of carbonic acid, a still smaller quantity of ammonia, and occasional traces of other gases.

Since the plant stores up oxygen within its cells at certain periods, it can scarcely be doubted that this gas fulfils some important office; but, excepting in the case of the germination of seeds, we have little information upon this subject.

It has been doubted whether any of those vegetable principles which contain nitrogen derive that element by direct assimilation of the gas existing in the atmosphere. Ammonia is looked upon

* The substance of two papers read before the British Association at the meetings of 1850 and 1851.

as the source whence it is obtained; but when the minuteness of the quantity is taken into account, the assimilation of nitrogen by plants, though improbable, may certainly still be held an open question.

It is to the decomposition of the carbonic acid in the atmosphere that vegetables are mainly indebted for the carbon which forms the basis of their structure.   The proportion of carbonic acid in the air in which different plants will thrive has engaged the attention of many experimenters, and is still the subject of investigation.   This at least is clearly ascertained, that, unless in strong sunshine, plants are destroyed by being placed in an atmosphere of pure carbonic acid.

The aqueous vapour in the air not only supplies hydrogen and oxygen to the organized vegetable structure, but serves many other purposes of a more physiological character.

We proposed examining the growth of plants when exposed to the action of gases that do not occur in the normal atmosphere, or of the ordinary gases in very unusual proportions.

Our first experiment was made with hydrogen gas.   A pansy was placed in an atmosphere consisting of 95 per cent. of hydrogen and 5 per cent. of carbonic acid.   The glass vessel in which it was confined had a capacity of 53 cubic inches.   It was inverted over water, so that connexion with the outer air was entirely precluded, and yet there was very little surface of water exposed to the artificial atmosphere within.   A little additional carbonic acid was introduced from time to time to replace that absorbed by the liquid.   The plant when first experimented upon had one blue flower in full bloom and one in the bud; for the first ten days the bud was gradually opening; but a slight mouldiness then came on, which increased during the next fortnight, by which time the plant having drooped decidedly, it was thought unnecessary to prolong the experiment. For the sake of comparison another pansy was placed in a glass vessel filled with atmospheric air, all other circumstances being equal : the plant became mouldy at about the same period as the other ; but the mould did not advance beyond the lower leaves, and the plant continued healthy for weeks.

Two flowering grass-plants (*Poa annua*) were placed in vessels of the same character and capacity as in the preceding experiment, and protected from the external air in the same manner. The one vessel was filled with pure hydrogen gas, the other with common air.   The plants grew and appeared healthy for about a fortnight, when mouldiness supervened in each instance.   Thus the substitution of unmixed hydrogen gas for the normal atmosphere produced no visible alteration.

The next experiment was with a mixture of hydrogen and

oxygen gases, the vegetable being supplied, as in nature, with the carbonic acid necessary for its growth through the agency of animal life. A large glass receiver capable of containing 177 cubic inches was filled with oxygen and hydrogen in the proportion of two measures of the latter to one of the former gas, in fact, in exactly the proportions requisite to form water. Into this atmosphere was introduced a pansy in flower, together with a few common house-flies and some sugar, and it was kept from communicating with the external atmosphere by being placed over water. A precisely similar arrangement was made in another receiver of similar capacity, but with the normal atmosphere in place of the mixed gases. It was anticipated that the plant would derive its nutriment from the aqueous vapour, and the carbonic acid produced by the respiration of the flies, while these again would feed upon the sugar; and we should thus have the same balance between the vegetable and animal kingdoms as obtains in nature, except that the animal would not feed upon the very plant which its breath nourished, a circumstance which it was obviously necessary for us to avoid. Besides ascertaining whether the pansy would flourish in mixed hydrogen and oxygen gases—the direct object of this experiment—it would afford an opportunity of observing any effects which the unnatural atmosphere might have upon the insects themselves. The pansy continued in a healthy condition for some time. As to the flies, it did not appear that the substitution of hydrogen for nitrogen in the atmosphere had any marked immediate effect upon their breathing; and thus the observations of M. Regnault upon other living creatures were confirmed by an instance drawn from the Articulata. But it was curious to observe the effects that resulted from the low specific gravity of the gaseous mixture. The larger flies when first introduced found themselves unable to walk up the glass, nor when they shook their wings did it assist them in mounting into the air; if they launched themselves from any prominent object, it was only by a great effort that they were able to fly an inch or two before falling to the bottom. While the comparative experiment made with atmospheric air presented a scene of animation by the rapid evolutions of the winged insects, and their buzzing against the glass which confined them, the flies walked slowly and in perfect silence about the interior of the vessel containing mixed hydrogen and oxygen.

Experiments were made in nitrogen gas. A pansy in flower, a young stock, and a grass-plant (*Poa annua*) in flower, were placed in atmospheres of this gas with the same arrangements as in the preceding instances. Another young stock was placed in air under similar circumstances for the sake of comparison: it was thought unnecessary to repeat the comparative experiment

with the others.   The pansy and the stock dried up and died in the course of a day or two; but the grass-plant grew and seemed healthy for several weeks, mouldiness only appearing on partially decayed portions.   We surmised that the deleterious effects of this gas, which we as well as other experimenters had observed, might be attributed to the phosphorus vapour which it always contains when prepared by the usual method.   Accordingly, we have subsequently employed pure nitrogen gas evolved by the mutual action of nitrite of potash and chloride of ammonium at a high temperature.   A pansy placed in this atmosphere under a glass vessel of 54 inches capacity inverted over water, remained flowering and vigorous for between two and three weeks.

It is curious to remark the readiness with which mouldiness grows in nitrogen gas.   A receiver half-full of nitrogen happened to be left standing over the pneumatic trough, and a bung was floating on the surface of the water inside.   In a few days' time a white growth was observed upon the bung; and not on it only, but also in patches over the surface of the water.   A bottle also partially filled with the gas was standing inverted in ordinary spring-water; the surface of the liquid inside was soon found covered with small patches of mould, which continued to increase.

A pansy and grass plant were placed in a receiver containing 180 cubic inches of pure oxygen gas, inverted as usual over water.   Both plants were in flower at the time of their introduction; they grew considerably taller, and the *Poa* showed extraordinary luxuriance in fructification.   After about twenty-four days the grass became mouldy, and the pansy drooped a short time afterwards.

Two similar plants were placed under a receiver of similar capacity, but filled with nitrous oxide.   In order to exclude the external air, the glass vessel was inverted over water saturated at the ordinary temperature with the same gas.   The water however gradually absorbed the nitrous oxide within, allowing it to diffuse into the atmosphere without; thus the liquid rose in the receiver, but it allowed of the continuation of the experiment for two months, during which time no extraordinary effect upon either plant was observable.   Davy records a trifling experiment upon a sprig of mint, which, so far as it went, indicated the innocuous character of his laughing gas; and Drs. Turner and Christison * found that 72 cubic inches of this, mixed with air in a vessel of 509 inches capacity, produced no visible effect upon a mignonette plant in forty-eight hours.   They do not appear to have pursued the investigation further.

The same experimenters concluded that carbonic oxide is probably of the same class of gaseous poisons, in respect to plants,

* Brewster's Journal, January, 1828.

as sulphurous acid or cyanogen, but that " its power is much inferior." They found that 23 cubic inches of carbonic oxide, with five times the volume of air, had no apparent effect upon a mignonette plant in twenty-four hours, but that it drooped when removed from the abnormal atmosphere. We imagine that the death of this plant must be ascribed to some other cause, since we have kept a pansy in a healthy condition for four weeks in 53 inches of pure carbonic oxide gas.

It order to ascertain what effect different gases might have in accelerating or retarding germination, and what compounds of carbon were capable of affording nourishment to the young plant, four onions just commencing to sprout were taken, weighed and placed in vessels containing respectively carbonic acid, carbonic oxide, coal-gas collected by displacement, and atmospheric air containing eight per cent. of light carburetted hydrogen prepared by the decomposition by heat of an alkaline acetate. The four vessels containing these bulbs were each capable of holding 53 to 54 cubic inches of gas, and were inverted over water as in the previous instances. The water employed to prevent access of air to the vessel containing the carbonic acid was itself saturated with the same gas ; that employed for the hydrocarbons was an alkaline solution, so as to absorb any carbonic acid which might happen to be present in the gas, or which might be generated by the growing root itself. A comparative experiment was made with another onion placed under a glass shade under similar circumstances as to light, heat, &c., but open to the atmosphere. The onions selected had each a plumule of about half an inch in length, and the experiments extended through the months of April, May, and June. The onions in the atmospheres containing hydrocarbons grew rapidly, and put forth fresh roots. After thirty days the plants were taken out of the coal-gas and carburetted hydrogen, as they had grown to the top of the vessels, being at the time in a very healthy condition. The onion in air grew, but not so fast. Those placed in carbonic acid and carbonic oxide stopped growing, and eventually became rotten. In each instance they lost weight.

In the early part of the year a crocus commencing to sprout was placed in a jar containing 70 cubic inches of carbonic oxide mixed with 100 cubic inches of atmospheric air, inverted over alkaline water so as to absorb any carbonic acid that might be formed. The rootlets of the bulb dipped into clear water. The crocus grew and put forth abundance of long leaves, but it never flowered. After remaining in this state for fifteen weeks, the experiment was discontinued, and the bulb and plant were found to weigh 285 grains, which was one grain less than at the commencement of the experiment. The gas within the receiver

decreased very much in volume, but was beginning to increase again towards the close, when the plant was becoming unhealthy in appearance.

A precisely similar experiment was made with light carburetted hydrogen prepared from the acetates in the place of the carbonic oxide : the growth of the plant was similarly affected, but it proved that this gas (at least in the proportion of seven parts of carburetted hydrogen to ten of air) is not poisonous to the bulbous-rooted plant in question. We have not performed any experiments with unmixed carburetted hydrogen or olefiant gas ; it is to be expected, however, that they would be found equally innocuous with carbonic oxide, hydrogen, and others which have been examined. Drs. Turner and Christison found no deleterious effect in twenty-four hours from a mixture of $4\frac{1}{2}$ inches of olefiant gas, with 100 times as much air. The action of gaseous hydrocarbons upon plants is a separate branch of inquiry, as it involves the interesting question as to whether these gases are capable of being assimilated or decomposed by the living organism of the vegetable, and thus of contributing to its support.

There is a peculiar circumstance attending the growth of the plants in most of the experiments above detailed, as also in the comparative ones made with atmospheric air,—a circumstance which may be constantly observed in " Ward's Cases," though perhaps not in so striking a manner. It is this :—they increase at first somewhat in height, and the leaves or flowers may open a little further than when first placed in the confined atmosphere, but after a day or two their growth appears retarded without any signs of decay. Thus in the experiment with the crocus in mixed light carburetted hydrogen and air, the bulb was placed in the inverted vessel on Dec. 27th ; rootlets and leaves of about 5 inches in length speedily shot forth, but then the functions of the vegetable seemed suspended, and it remained in the month of July just as it was in February, a crocus with delicate green leaves opening for the protrusion of the flower-stalk.

These results indicate that gases may be divided into two great classes in respect to their action upon vegetable life ; namely, those which are decidedly poisonous, and those which exert no deleterious influence. The poisonous gases have been investigated by Drs. Christison and Turner in the memoir already adverted to more than once ; they are sulphurous acid, sulphuretted hydrogen, hydrochloric acid, chlorine, and cyanogen ; and a very minute quantity of any of these is found to destroy plants immersed in them for only a few hours ; indeed some of them, sulphurous acid for instance, are decidedly more injurious to vegetable than to animal life. In respect to hydrogen, Davy came to the conclusion that it was injurious to some plants, but

not to others ; Saussure found that a plant of *Lythrum Salicaria* flourished for five weeks in an atmosphere of this gas. Is it not possible that some of the compound gases which frequently contaminate hydrogen, and which are known to be poisonous even in very small proportion, may have led to the destruction of those plants which died apparently through the influence of hydrogen gas ? As far as our own experiments are concerned, we find hydrogen, nitrogen, oxygen, carbonic oxide, nitrous oxide, and perhaps gaseous hydrocarbons, to be perfectly innocuous to vegetable life in any proportion.

The earth's atmosphere is common to all the tribes of organized existence which inhabit the land, whether fixed to one locality or endowed with voluntary motion ; but its component gases perform different functions in respect to the two great classes into which we are in the habit of dividing them. No animal, as far as we are aware, can exist for any length of time in an atmosphere devoid of oxygen, whilst on the other hand all those which are usually included under the appellation of the " vegetable kingdom " are dependent for their food upon those gases which contain carbon. We know from Regnault's experiments that the amount of oxygen in the air may vary largely, and that the nitrogen may be replaced by hydrogen gas without any marked effect upon animal life ; and we now find even more strikingly in regard to plants, that either of the great constituents of the atmosphere may prevail to the exclusion of the other, or that they may be replaced by totally different gases, without involving the destruction of the living organism ; of course they cannot increase in substance without carbonaceous food, yet the deprivation of this appears only to lead to an indefinite suspension of their functions. Doubtless the actual constitution of the atmosphere is that which is most suited to the permanent well-being of the whole of the organized creation, and perhaps it is equally requisite both for plants and animals ; yet it is evident that great deviations from its normal constitution may take place without producing serious injury.

ON THE

INFLUENCE OF THE SOLAR RADIATIONS

ON THE

VITAL POWERS OF PLANTS

GROWING UNDER

DIFFERENT ATMOSPHERIC CONDITIONS.

By J. H. GLADSTONE, Ph.D.

On the Influence of the Solar Radiations on the Vital Powers of Plants growing under different Atmospheric conditions. By J. H. GLADSTONE, *Ph.D.*

THERE are few subjects of experimental research in which such opposite statements have been made as on the mutual action of the atmosphere and the vegetable kingdom; even the apparently simple question as to whether plants increase or diminish the amount of oxygen in the air was long a matter of dispute. This arose partly from defective modes of analysing gases; partly from experiments upon plants being made under circumstances very unfavourable to their healthy development; and partly also from variations in light having a great influence in modifying the functions of the vegetable world. The history of these discussions, in which many of the greatest philosophers of the day took part, is too long and too well known to need further notice here. When it was fully conceded that carbonic acid really is decomposed by the plant, it was natural enough that those who observed the wonderful powers of the chemical rays of the solar spectrum in reducing salts of silver and other substances, should refer the chemical changes taking place within the vegetable tissues to the same occult agency. But Dr. Daubeny, in an admirable investigation, published in the Philosophical Transactions for the year 1836, has shown by indisputable evidence that it is the luminous, and not the chemical or the calorific rays, which cause the decomposition of carbonic acid with emission of oxygen from the leaves, the formation of chlorophyl, the irritability of the *Mimosa*, the evolution of water, and indirectly at least the absorption of it by the roots. The colours of flowers are supposed by this author to depend also on the luminous rays; sunshine was found to act far more energetically than diffused daylight, while no colouring effects were observed to be produced by any artificial illumination, not even by that afforded by incandescent lime.

That portion of the inquiry requested by the British Association which devolved upon me, embraced a question not included in the investigations of the Oxford Professor, nor in those of any other experimentalist, as far as I am aware: I refer to the influence of various atmospheric conditions in conjunction with light. This circumstance necessitated the employment of closed vessels under which the plants should be grown; and glass, from its transparency, was not only the best but almost the sole article which could be employed. Bell-shaped glasses were accordingly procured; and they were made of various colours, in order that the different properties of the spectrum might be to a considerable extent separated.

The blue glasses mentioned in this paper had each a capacity of about 690 cubic inches. A smaller bell-glass of 172 inches capacity was also employed in an experiment not described on the present occasion. The yellow glasses had a capacity of 650 cubic inches; the red of 558; and those made of colourless glass of 740 cubic inches. The darkened glasses mentioned below were made by partially covering bell-jars with brown paper, thus excluding the light except such as passed through about one-eighth of the surface of the glass, and that on the side turned away from the window. Their cubic

contents were 500 inches. Small colourless and yellow glasses were also procured, each having a capacity of 177 cubic inches.

The blue glass employed is of so intense a colour, that it cuts off by far the greater portion of the luminous rays, but photographic paper showed that it admits the chemical rays freely; it may also be considered as interfering much with the transmission of heat. The red glass, on the contrary, freely admits the calorific influence, but stops the chemical, whilst, like the blue, it diminishes greatly the luminous. The yellow again scarcely decreases the illuminating power of light, but almost destroys its chemical action.

The place in which the experiments here described were conducted, was a room in a dwelling-house at Stockwell, in the neighbourhood of London. The glasses stood on a table close by the window, which had a S.S.E. aspect. No fire was ever lighted in the room, but it must have been a little warmer than the external atmosphere in the winter time on account of the vicinity of heated apartments.

As preliminary experiments, merely the effect of these coloured glasses in accelerating or retarding the growth of various kinds of plants was tried.

Hyacinths were chosen as samples of bulbous-rooted plants. They were all of the same description, purple in colour, as nearly as possible of the same size, healthy, and beginning to put forth a plumule and radicles. They were weighed, placed on the top of colourless glasses containing sufficient pure water just to touch the rootlets, and then covered with the large glass shades. The experiments were started on Nov. 13th. In order to change the air, the shades were lifted off for a minute or two about every second night. Each plant grew healthily and flowered; yet some differences were observed of a character which might fairly be attributed to the quality of the light. First, as to the rootlets. Under the colourless glass they grew abundantly; under the blue glass they also grew abundantly and more rapidly; under the red glass scarcely any rootlets were produced, and what there were never attained any considerable length; while under the yellow glass they were few in number, but long. Secondly, as to the leaves and flower-stalk. Under the colourless glass they were put forth in process of time and grew healthily. No difference was noticeable under the blue; under the red long spreading leaves were put forth, that bent towards the light in a very marked manner, and the plant had an unhealthy appearance; while under the yellow glass short sturdy leaves and flower-stalks were produced.

As to the flower itself, it began to open at about the same period in each instance, namely,—

> Under colourless glass, on Feb. 11th, or after 90 days.
> Under blue   ,,   ,,   10th, ,,   89 ,,
> Under red   ,,   ,,   8th, ,,   87 ,,
> Under yellow   ,,   ,,   10th, ,,   89 ,,

There was no observable difference in the colour of the four flowers, notwithstanding the variety of tint under which they had been formed. The flower under the red glass was long and thin. Latterly they all suffered for want of room.

On April 16th all the plants were removed from the water into which their rootlets dipped, dried in the air, and weighed.

		Primary weight of bulb.	Weight of fully developed plant.
Under colourless glass		1305 grs.	2118 grs.
Under blue	,,	1328 ,,	2026 ,,
Under red	,,	1135 ,,	1386 ,,
Under yellow	,,	1299 ,,	1704 ,,

showing an increase of—

Under colourless glass, as	1000	:	1623
Under blue ,,	1000	:	1525
Under red ,,	1000	:	1221
Under yellow ,,	1000	:	1312

The greatest growth therefore was in the plant exposed to all the influences of the solar ray.

Cereals were also grown under the various glasses, a comparative experiment being made under a darkened shade. Access of air was permitted to the plants by the glasses being placed upon boards which were perforated with holes close together, and were raised about one-third of an inch from the table. No direct rays of light could enter, especially as the space under the boards was blocked up on the side nearest the window, and any diffused light finding access by the perforations had to pass through several folds of tarlatane of the same colour as the glass shade itself.

On Sept. 12th three grains of white wheat, sown in garden mould, to which a little stable manure was added, were placed under the various glasses. The wheat began to grow in a few days in each instance, one seed only under the red glass proving unproductive. They were watered as occasion required. In a week or two the plants under the darkened shades attained a considerable height, turning in a very marked manner to that part where most light entered. No secondary leaves ever appeared, but each plant consisted of two long white leaves of about 9 inches in length, so thin and flaccid that they were unable to support themselves; and after thirty days they drooped entirely and became mouldy. The corn-plants under the other glasses grew more slowly, but put forth many leaves, attained a height of 10 or 12 inches, and remained healthy throughout the winter and spring. Those under the yellow glass were the most sturdy in their growth; and those under the blue alone appeared thin and unhealthy.

Mallow-seeds (*Malope trifida*) were sown in garden mould, and placed under the various glasses near the commencement of September, the arrangements being the same as in the preceding experiment. They began to grow after the lapse of a few weeks, first under the colourless glass, then under the blue, and afterwards under the red, yellow, and darkened glasses at about the same time, October 8th. Thin etiolated stalks, with only the first pair of leaves, and those badly developed, about 2 inches in length, were all that was produced under the darkened shade. In about a fortnight they died; and in the middle of March some other seeds sprouted in a precisely similar manner. The mallows under the other glasses grew more healthily and survived much longer, but in no instance did they arrive at maturity: the best plant was one that grew under the yellow light; it had sprouted in the early part of January and put forth many leaves, reaching the height of 5 inches. They grew worst perhaps under the blue glass. A self-sown *Stellaria* grew luxuriantly along with the mallows under the red, and a grass-plant under the yellow shade.

In a paper read by my brother and myself before the Association last year, and published in the Philosophical Magazine for September 1851, we remarked that plants kept in an unchanged atmosphere appear to enter into a sort of lethargic condition. An experiment was instituted for the purpose of ascertaining whether the alteration in light produced by coloured media made any marked variation in this matter; and as the pansy and *Poa annua* were the plants generally experimented on in our previous investigation, they were employed here likewise. Six pansies newly struck, which had

taken good root and were vigorous, were planted in six flower-pots containing good garden mould; and with each was also placed a grass-plant in flower. They were all set in trays filled with water to the depth of an inch, or thereabouts; five were covered with the different descriptions of glass shades dipping into the water, so as to cut off all communication between the external and internal atmospheres; while one was freely exposed to all the changes of the surrounding air. The experiment was commenced on October 17th, and access of air was never permitted to the covered plants. The results under the glasses were very various, but how far they depended upon the character of the light or upon the peculiar atmospheric condition, could not be determined with any accuracy. One thing however was clear, that the plants survived much longer for being in an unchanged atmosphere. The pansy that was not covered by any shade was attacked with aphides eight weeks after the commencement of the experiment, and although these were washed off, it drooped before the end of December. The *Poa* also scarcely survived the winter. Under the colourless glass the plants remained healthy much longer; the pansy was attacked by the forementioned insects at the commencement of December, but although it was necessarily impossible to remove the aphides without disarranging the experiment, the plant lived till March. The grass-plant grew very luxuriantly. A curious phænomenon was observed. As the air within the glass shade was perfectly still, the ripe seeds of the *Poa* did not fall from the flower-stalk, and through the dampness of the atmosphere many of them which rested against the sides of the glass germinated and shot forth leaves, in some instances 3·5 inches long, and radicles of 1 inch in length. Under the blue shade the plants grew very tall. No aphides appeared, but mouldiness was observed. In March both plants were straggling and unhealthy; the grass-seeds never germinated; and any portion that died quickly suffered decomposition. The plants exposed to the red light were healthy at first, and the grass grew luxuriantly; but aphides appeared on the pansy in the middle of December, and at the commencement of the succeeding month it became sickly and drooped. The grass-plant also lost its healthy appearance during the spring: some of its seeds germinated. Under the yellow glass neither of the plants increased in size at first, but in the spring they grew, the grass attaining a very great length; they maintained a strong and healthy appearance; no insects showed themselves on the pansy, and the grass-seeds gave little indications of germinating. Some changes in the colour of the pansy's leaves were observed to take place, but the grass remained of its proper green tint. The plants under the darkened shade soon became sickly. On December 11th the grass was found to be dead; the pansy had grown tall, and turned decidedly towards the least darkened part of the shade; it was mouldy and ill-favoured, and on January 6th it drooped.

Researches connected with the growth of plants must necessarily stretch over a considerable space of time. My object in detailing these experiments now is not to draw any general conclusions from them; I regard them as far too few and uncertain for that; but offer them to the Association as a sample of my preliminary attempts in this inquiry,—attempts which may indicate a line of fruitful investigation in future seasons.

ON THE

INFLUENCE OF THE SOLAR RADIATIONS

ON THE

VITAL POWERS OF PLANTS

GROWING UNDER

DIFFERENT ATMOSPHERIC CONDITIONS.

PART II.

By J. H. GLADSTONE, Ph.D., F.R.S.

On the Influence of the Solar Radiations on the Vital Powers of Plants growing under different Atmospheric Conditions.—Part II.
By J. H. Gladstone, *Ph.D., F.R.S.*

Since I laid before the British Association my former Report, some of the experiments there detailed have been repeated, and the investigation has been pursued further in the same direction. I have the honour now to present the results which have been obtained.

The experiments about to be described were conducted, not as before at Stockwell, but in Tavistock Square, London. The locality was not quite so favourable to the growth of plants, but they had always the advantage (unless otherwise stated) of standing on tables at the windows of a large upper room having a south-east aspect, so that they obtained the full benefit of the morning and noonday sun. The apartment was never artificially heated, but in the winter time it must have been a few degrees higher in temperature than the external atmosphere.

The coloured bell-glasses described in the previous Report were made use of. I am now able to give a more accurate description of what solar rays were actually transmitted by them. The effects of the different glasses on the prismatic spectrum were as follows:—

Colourless glass. No perceptible difference from the normal spectrum.

Yellow glass. The red rays were cut off, but the line C was just visible in the orange-coloured region. The yellow and green portions of the spectrum were quite natural, except perhaps that they were rather more uniform in colour than usual; the blue was rather bright above the double line F, but there was very little illumination in the portion more refracted, and the violet rays were quite unseen. The lines D, E, *b*, and F were very visible.

Red glass. The spectrum consisted of two luminous spaces, separated by a broad band of perfect darkness. The one was of a red and orange colour, commencing between B and C, and apparently cut off by the dark line D. The other was faintly illuminated with an olive-green tint, commencing about the most intensely yellow part of the ordinary spectrum, and continuing to about *b* (which was barely visible), and then passing into a lilac hue, which gradually faded off, till it became imperceptible perhaps a little below the lines F.

Blue glass. The spectrum had a very singular appearance, consisting of several distinct luminous bands. First there was a reddish band of considerable brilliancy, occupying a space beyond that of the least refrangible portion of the visible spectrum. This was separated by a dark space from a very narrow but bright band somewhere near the line B. Its colour was very different from any of those of the normal spectrum, but perhaps it approached nearest to the orange. Then, after another dark space, came a bright yellow band of greater width, just above the line D, which, however, was not itself perceptible. The whole yellow portion of the spectrum was cut off, and there was no illumination till about midway between E and *b*, where a bright green suddenly appeared. This passed into a pale green, where there was very little illumination, but not perfect darkness, till at about F an intense blue appeared, continuing through the region of the violet, to the end of the most refrangible portion of the spectrum. The lines *b*, F, and G were very distinct, as well as some about *d* and H.

This analysis of the light transmitted by the various glasses, confirms the description previously given of their character, namely, that "The blue glass cuts off by far the greater portion of the luminous rays, but admits the

chemical rays freely; it may also be considered as interfering much with the transmission of heat. The red glass, on the contrary, freely admits the calorific influence, but stops the chemical, whilst, like the blue, it diminishes greatly the luminous. The yellow again scarcely decreases the illuminating power of light, but almost destroys its chemical action."

The series of experiments on hyacinths, which was described in the last Report, was repeated with additional attention to the effects of partial or complete darkness. The large colourless, blue, red, and yellow bell-glasses were employed, together with a partially obscured colourless shade, and a partially obscured yellow shade; and another experiment was instituted under a glass shade placed in a large box, so that the light was completely excluded, except when for a few moments the lid might be removed for the purpose of observing the progress of the experiment. As in the preceding experiment, the bulbs were all of the same description, of a healthy appearance, and of about the same size. After being weighed, they were placed as before on the top of colourless glasses, filled with pure water, and covered with the large bell-jars. In this case the jars were themselves placed upon the perforated boards, with the arrangement of tarlatane, &c., mentioned in the previous paper. The experiments were commenced on December 10th; each of them was successful; the results accorded in some points with those of the former occasion, but in other respects there was considerable discrepancy. The experiments made in partial or complete obscurity were perhaps the most instructive.

Rootlets began to appear immediately under the dark shade, and on December 26th, that is, after sixteen days, they were found to be $1\frac{1}{2}$ inch in length. They grew rapidly, and were very numerous. They were thin and long, and appeared to have little strength. Under the obscured colourless and obscured yellow glasses, the rootlets also began to grow quickly, becoming three-quarters of an inch long in a fortnight's time; while under the blue and colourless glass exposed to the full power of the light, the rootlets did not so quickly attain any length, and in the same space of time there was scarcely anything observable under the red or yellow glass. The roots continued to grow under the obscured glasses until the beginning of February, but they arrived more rapidly at maturity under the influence of the white and blue light. Under the red shade the roots never attained any considerable length, but they were stout and strong. Under the yellow shade there was scarcely any growth below the bulb until near the end of January, when a few long straggling roots made their appearance. This is very accordant with the effect that was observed during the previous season to be produced by the coloured glasses. This shows that the development of the root takes place most rapidly in the absence of all solar radiations; that partial obscurity is also favourable; that the less refrangible rays of the spectrum had especial power to retard their growth, and that the luminous and calorific rays had peculiar actions of their own.

As to the leaves, little appearance of growth was observable in any of the hyacinths till December 26th, when those under the colourless and blue glasses began to shoot; that under the red glass followed very soon, while those under the yellow and the partially and wholly obscured glasses gave no sign for about three weeks longer. The leaves grew most rapidly in the blue light. The following comparisons of the length of the leaves under the various luminous influences may be interesting. They were taken on the 13th and 21st of February, when all the plants were in vigorous growth, but not one of them had flowered, and on March 22nd, when the plants had attained their full maturity.

	February 13.	February 21.	March 22.
Under the colourless glass	4 inches	6 inches	11 inches
„ blue „	6 „	8 „	14 „
„ red „	3 „	5 „	11 „
„ yellow „	2 „	3 „	8 „
„ obscured colourless glass	3 „	3½ „	10 „
„ obscured yellow „	3 „	3½ „	12 „
„ dark glass	3 „	4 „	10 „

The flower-stalk very nearly kept pace with the leaves. There was a greater difference in the periods at which the petals opened than in the former series of experiments; those under the blue and colourless glasses took the lead, and those under the partially obscured glasses were the last. They opened for the most part during the last days of February. Under the red shade two flowers grew, but they were thin and straggling : the same was the character of the plant that grew in the dark. There were two flower-stalks under the partially obscured colourless glass; they were never developed, however, but were found at the end of March losing their colour and becoming rotten. The experiments were terminated on March 22nd, excepting the two under the partially obscured glasses, which were allowed to continue till the 30th. The respective lengths of the flower-stalks were then,—

Under the colourless glass..................	13	inches.
„ blue „	13	„
„ red „	12·5	„
„ yellow „	12	„
„ obscured colourless glass	4	„
„ obscured yellow „	10	„
„ dark „	13	„

The hyacinths having been removed from the water in which their roots had been immersed, were suffered to dry in the open air of the room for twenty-four hours, and were then weighed.

	Primary weight of bulb.	Fully developed plant.	Actual increase.
Under the colourless glass	936 grs.	1494 grs.	558 grs.
„ blue „	862 „	1472 „	610 „
„ red „	856 „	1438 „	582 „
„ yellow „	1008 „	1406 „	398 „
„ obscured colourless glass	873 „	1591 „	718 „
„ obscured yellow „	872 „	1556 „	684 „
„ dark glass	763 „	1205 „	442 „

If, instead of observing the actual increase of weight, we compare the original weight of the bulb with that of the fully developed plant, we obtain the following proportions :—

Under the colourless glass as	1000 : 1596.
„ blue „	1000 : 1708.
„ red „	1000 : 1680.
„ yellow „	1000 : 1395.
„ obscured colourless glass as	1000 : 1822.
„ obscured yellow „	1000 : 1784.
„ dark „	1000 : 1579.

This increase in weight in the growing hyacinth is due to the fixation of water, and not to the decomposition of carbonic acid in the atmosphere; at least a smaller bulb which was placed under a colourless shade, and cut off from the external atmosphere by the edges of the glass dipping into water, grew and flowered perfectly well; and when removed from the shade on March 22nd, and dried as the others were, it gave the following weight:—

Primary weight of bulb.	Fully developed plant.	Actual increase.
625 grs.	1167 grs.	542 grs.

or as 1000 : 1867,—

a larger proportional increase of weight than in any of the other experiments, the actual increase being about the same as that of the other plant which grew under the colourless glass.

The leaves that grew in the dark were perfectly etiolated, excepting just at the tips, where they showed the normal green colour gradually shading off as it descended. The leaves that appeared in the experiments with the obscured glasses, were somewhat lighter in tint than those growing where the direct radiance of the sun could find access. The character of the light, under which the flowers were grown, did not affect their colour at all in the way that might have been expected. They were all, as on the former occasion, of an equally deep purple; even that which grew in complete darkness exhibited the same depth of colour in all the petals, excepting a few of the lower ones. The purple flower under the colourless glass when fading turned to red; and this was also the case under the blue and yellow glasses; but the flower under the red glass showed no trace of red colour, even when it had quite shrivelled up, nor was there any such change in the intense purple that appeared where light was excluded.

In such experiments as those just detailed, it is difficult to separate what might be the effect of adventitious circumstances from the genuine effect of the diversity of light. However, we may safely remark in the experiment which was conducted in perfect obscurity—the rapid and abundant growth of thin rootlets, the general healthiness of the plant, the non-formation of chlorophyll, but the production of the colouring matter of the flower, not altered in its subsequent fading. The two experiments performed in partial obscurity appeared as closely alike as possible, until the last week, when one of the plants died. The fact that the chemical rays were cut off from one of them, made no apparent difference. Their backwardness, as compared with the other flowers, was probably owing to their having been placed in a position which was somewhat colder than that of those which received the full light of the sun. The effects of obscurity were observable in them in a modified manner, and they both absorbed much more water than the other plants did. The effect of the red glass in interfering with the length of the roots, and in producing a badly developed plant, was observed both in this and in the former series of experiments. Its power of preventing the reddening of the faded flower is remarkable. The effect of the yellow glass in causing the rootlets to be few and straggling, and in diminishing the absorption of water, was also noticed in both instances. The blue glass appeared to favour the development of the hyacinth.

That the green colouring matter of leaves requires the action of light for its production, has long been universally admitted, and Dr. Daubeny has shown that it depends on the luminous ray. From analogy, and from a few observations by Davy, Senebier, and others, the same has been assumed to hold good in respect to the colours of flowers, but the purple hyacinth bears other witness, and should induce us to doubt this too hasty conclusion.

A number of experiments on germination were made during the spring.

The seeds experimented on were those of the wheat and the pea; and in every case both were employed, in order that if there should be a different effect of light on the monocotyledonous and dicotyledonous plants, it might be seen. Seeds of familiar plants and of great commercial importance were chosen, as it was supposed a greater degree of interest would naturally attach to experiments on them, and it might happen that some observations of value to the agriculturist might be made.

The first series of experiments was made in common air, under the seven various influences of coloured light and obscurity which have been described in treating of the hyacinths. The coloured shades were arranged before the windows, as described above, and they dipped into plates of water, so that throughout the experiments they were filled with an unchanged atmosphere, saturated with moisture. Twelve grains of wheat and twelve peas were taken for each separate experiment, and their weight was noted while they were still dry. They were placed on bricks within the glass shades, the bricks standing in the water, so that they were always damp. Another arrangement was made, similar to that just described in every particular, except that the seeds were in the open air of the room, without any cover.

The experiments were commenced on April 21st. The following is a table of the weather, and of the temperature taken in the shade at mid-day during the time that the various experiments with peas and wheat continued:—

April 22.	cloudy		May 15.	fine	69°
,, 23.	do.		,, 16.	variable	65
,, 24.	do.		,, 17.	fine	66
,, 25.	variable		,, 18.	cloudy and wet	64
,, 26.	do.	60°	,, 19.	fine	66
,, 27.	wet	57	,, 20.	do.	67
,, 28.	variable	56	,, 21.	....	...
,, 29.	do.	56	,, 22.	cloudy and wet	64
,, 30.	....	...	,, 23.	fine	65
May 1.	wet	55	,, 24.	variable	63
,, 2.	variable	55	,, 25.	fine	66
,, 3.	do.	59	,, 26.	do.	67
,, 4.	fine	61	,, 27.	wet	63
,, 5.	variable	63	,, 28.	....	...
,, 6.	cloudy	60	,, 29.	wet	63
,, 7.	....	56	,, 30.	do.	63
,, 8.	variable	...	,, 31.	fine, but cloudy	65
,, 9.	wet	60	June 1.	fine	66
,, 10.	fine	58	,, 2.	wet	63
,, 11.	cloudy	62	,, 3.	fine	65
,, 12.	fine	60	,, 4.	....	...
,, 13.	cloudy	64	,, 5.	cloudy	63
,, 14.	....	65	,, 6.	do.	63

We shall first consider the growth of the wheat; afterwards that of the peas; and then compare the two.

On April 26th the corn-seeds were found just beginning to burst under all the seven glasses, those under the obscured yellow being the most advanced. Further growth was visible the following day under that glass, and also under the obscured colourless, and the yellow, though the plume did not appear in any case till the 29th. On May 1st the radicles under the colourless and blue glasses were of considerable length, but those under the obscured colourless and the red were longer, while the longest were under the yellow glass. On April 29th plumes appeared under the red and obscured colourless glasses, and in the dark. They appeared two days later

under the colourless and the blue, while the seeds under the obscured yellow had an unhealthy look. On the 4th of May long etiolated leaflets were found in the dark; under both obscured glasses the wheat had also shot up long leaves; under the red and yellow glasses there were plumes of 1 or 2 inches in length; while under the colourless and blue they only reached half an inch. The wheat-plants under the colourless glass then began to grow more rapidly, and soon gained the advantage of those under the blue, and still more of those under the red. On the 8th they measured 3 inches, while those that had grown in the dark measured 6.

On the 12th the wheat-plants were more fully examined, and drawings of them were made. It was then found that under the colourless glass ten of the twelve seeds had grown. They presented very uniformly the appearance given in Plate IV. fig. 1,—leaves erect, of a full green colour, from 4 to 5 inches in height, roots long and thin, five in number, taking firm hold of the brick. They had no side rootlets, but were fringed with hairs. Under the blue glass, the wheat appeared like that under the colourless, but smaller. Under the red, only four plants grew like fig. 1, and they were not so regular in form, size, or general aspect as those under the colourless glass. Four others had grown somewhat like fig. 2, where there was this peculiarity,— the green stalk had been unable to burst the transparent membranous sheath, and had forced itself out in a kind of loop, at that part where the sheath sprung out of the seed. The roots were generally flaccid. Under the yellow glass, the radicles were so strong, and bent so decidedly downwards, that they raised the seed completely on end: they were thickly covered with hairs. The stalks were short and strong, and generally bent in the manner represented in fig. 3. Under the obscured colourless glass only seven seeds had germinated: they were all like fig. 4. The leaves were of a pale green colour, and had not succeeded in bursting the membranous sheath; the roots were very long. Under the obscured yellow glass, the plants were of a greener colour than the preceding; six of them were like fig. 3, excepting that the leaves were very much taller, perhaps 7 inches high. In the dark all the plants were weak, and of a very pale green colour, almost yellow; the radicles had many rootlets branching out from them; four were like fig. 5; two others were smaller and had second leaves, while other two were very short in the leaves.

After this, the plants under the colourless glass continued to grow healthily: the hairs along the roots became very long and thick, and on the 22nd of May, ramifications of the rootlets began to appear. The plants under the blue did not continue so healthy, nor did those under the red. Under the yellow glass, both the upper plant and the roots continued to grow. Under the obscured yellow glass and in the dark, the plants also continued growing. On the 26th, a more full examination and fresh drawings were made. Under the colourless glass there were ten wheat plants like fig. 6, generally 8 or 10 inches in height. Under the blue glass there were several very thin weak plants, only about 2 inches high. Under the red, the utmost development was to the extent of fig. 7, in the case of three plants. The rest that were growing had not succeeded in breaking the membranous sheath, but were contorted in their efforts to escape. Under the yellow, three plants had grown like those under the colourless glass; three others were not so fully developed, while the remaining four had not germinated. Under the obscured colourless glass, the wheat had not grown since May 12th. Under the obscured yellow, I found six plants like fig. 8. In the dark, the plants had grown much as under the obscured yellow glass, but they were still longer, weaker, and paler in colour.

On June 5th, the experiments were stopped. The plants under the colourless glass were healthy in every respect, and were of a better green than any of the others. Under the red glass, one of the plants was found to have shot up several small leaflets outside the transparent sheath, which it had been unable to pierce.

The following table shows the number of seeds of wheat which had put forth roots, and the average length of the principal roots; and also the number of seeds from which plants had grown, together with the average length of the principal leaves.

	Roots.		Leaves.	
	No. of plants.	Length.	No. of plants.	Length.
Colourless	10	2·5 inches	10	10 inches
Blue	6	0·75 ,,	6	4 ,,
Red	8	3·5 ,,	4	4 ,,
Yellow	7	2 ,,	6	9 · ,,
Obscured colourless	6	3·5 ,,	3	2 ,,
Obscured yellow	{ 6 / 2	0·75 ,, / 2·5 ,, }	7	8 ,,
Dark...	7	3 ,,	6	13 ,,

The plants were removed from the bricks, spread out on the table, and allowed to dry in the air for eighteen hours. The following table shows the weight of those which had grown under each of the various conditions of light. The original weight of the twelve corn-seeds was in each instance 8 grains, giving as the average weight of each seed 0·66 gr.

	No. of plants which had germinated.	Weight.	Average weight of each.	Average increase upon original weight.
Colourless	10	31 grs.	3·1 grs.	2·4 grs.
Blue	6	4 ,,	0·66 ,,	0 ,,
Red	8	4·5 ,,	0·56 ,,	−0·1 ,,
Yellow	7	8 ,,	1·1 ,,	0·4 ,,
Obscured colourless	6	4 ,,	0·66 ,,	0 ,,
Obscured yellow	7	10 ,,	1·4 ,,	0·7 ,,
Dark	7	9 ,,	1·3 ,,	0·6 ,,

The increase in weight of the plants which had grown under the colourless, the dark, and the yellow glasses, was due, of course, to the fixation of water, for there was no supply of carbonic acid from the air, and the quantity of substance which the roots could absorb from the bricks must have been very trifling.

The comparative experiment in which the seeds were exposed to the open air of the room did not come to anything. Not one of the seeds succeeded even in bursting the tunic, doubtless because the dry atmosphere prevented their ever retaining sufficient moisture.

The presence of soil about the germinating seeds, or a constant change of air, would probably have modified these results; yet the conditions observed in this series of experiments were thought necessary, in order to have the full effect of the different sorts of light about the seeds themselves, for a soil necessarily produces partial, if not total obscurity. The deprivation of other sources of carbon, beyond the cotyledons of the seed itself, also answered certain purposes. On examining the results, the following conclusions may be drawn, as far as wheat is concerned growing under the conditions of the

experiment. The absence of the chemical rays favours the first growth of rootlets, and the presence of the luminous rays does not impede it. Afterwards the opposite effect takes place; the roots are stopped in their development by the yellow ray much more than by all the rays of the spectrum in combination. The red or calorific ray is on the whole the most favourable to the growth of the roots, even more so than the complete absence of all solar radiations. The shooting forth of the plume is also favoured by the withdrawal of the chemical rays, especially just at first; but the full and healthy development of leaves requires all the rays of the spectrum, the luminous being particularly necessary. Several other peculiarities may be noted; for instance, the downward tendency of the roots under the pure luminous influence; the comparatively greater development and strength of the membranous sheath under the calorific agency; and the late but abundant growth of side-rootlets, where all the solar radiations were admitted.

The results of the experiments on wheat recorded in the previous Report, where there was the presence of soil and change of air, appear to indicate still more clearly the beneficial character of the luminous emanations, for the plants under the yellow shade were found even to excel those which had grown in white light, while, as in the experiment just detailed, the cutting off of the luminous ray by the deep blue glass militated greatly against the health of the plants. The protection of the rootlets from the yellow ray may be fairly considered an advantage, but a proper series of experiments on wheat-seeds surrounded by earth is still a desideratum.

We have now to consider the growth of the *peas* under the different solar influences. It has been already stated that twelve peas soaked in water were placed on the bricks along with the wheat seeds, on April 21st. On the 24th they were found to be swollen and beginning to burst. The seeds under the yellow, obscured yellow, and obscured colourless glasses, were the more rapid in their first development. On the 29th, the plumes began to appear under the obscured colourless, yellow, and red shades, and two days afterwards under the blue and colourless. The plants under the obscured yellow glass appeared very unhealthy. The radicles grew astonishingly under the yellow glass, and became very long under the red and obscured colourless. On May 8th, the plants in complete or partial obscurity were found to be several inches high; under the red, 2 inches; under the yellow, not quite so much; while even on the 11th, the plants under the blue had only just developed themselves, and under the colourless glass only one seed had put forth a stalk, and that was but half an inch in length.

On the 12th they were more fully examined, and drawings were made. Under the colourless glass, the peas resembled fig. 1, Plate V. the plume only in the first stage of development, the principal root short and thick, with short and thick secondary rootlets, all fringed with hairs. Under the blue, the peas were in a somewhat more advanced stage, like fig. 2. Under the red, ten plants had grown somewhat like fig. 3,—roots straggling, stalk bending towards the light, with many leaflets of a deep green colour. The plants under the yellow glass were characterized by enormous roots, as shown in fig. 4, which turned away from the light in a very marked way. Nine of those under the obscured colourless had the appearance presented by fig. 5,—long roots, long succulent weak stalks, and pale green leaflets. Under the obscured yellow, the plants appeared for the most part like fig. 4, but with smaller roots, though two of them, which were nearest the light, had grown with a stalk like that represented in fig. 5. In the dark, six of the peas had grown like fig. 6,—roots irregular, having few side-rootlets, stalks succulent, but tolerably erect, bearing yellow leaflets. The plants in

the red light continued to grow healthily, some being 6 inches high on the 15th; under the yellow and obscured yellow, they also grew healthily; under the obscured colourless, the stalks were found on the 22nd no longer capable of supporting themselves. The stalks in the dark were at the same time erect, and 10 inches in length. On the 26th, the seeds under the colourless glass were found to have made scarcely any advance since the 12th. Under the blue, one had grown tall and healthy, but the rest were very small. Under the red, the plants were growing healthily as on the 12th, but some of them had attained the height of 9 inches, and bore three or four secondary branches. Those under the yellow had grown, but did not appear healthy. Under the obscured colourless glass, the plants had grown since the 12th about as much as might have been expected from the time, but they were very weak. Under the obscured yellow glass there were two very similar to, and nearly as large as, those under the obscured colourless. Six others were of the same character, but much smaller; the roots were very short. The plants in the dark had also grown since the 12th.

On June 5th the experiments were discontinued. The longest pea-plant under the colourless glass was then only 1·75 inch in length; the secondary rootlets were remarkably short and thick. The plants under the blue appeared the most healthy; those under the yellow, whether in full light or obscured, showed considerable inclination to send out lateral branches. The stems of the plants in the dark were white, the leaflets were canary-yellow; those which had grown in partial obscurity were also much etiolated. One of the peas under the obscured yellow had produced a triple stem, and so had one of those under the obscured colourless glass, as drawn in fig. 7.

The average length of the roots and stalks of those peas which had germinated under the different solar influences is given in the annexed table :—

	Tap roots.		Stalks.	
	No. of plants.	Length.	No. of plants.	Length.
Colourless	10	1 inch	10	1 inch
Blue	{ 10 2	2 ,, 5 ,, }	12	7 ,,
Red	11	3·5 ,,	11	6 ,,
Yellow	{ 7 4	1·5 ,, 6·5 ,, }	10	6·5 ,,
Obscured colourless	10	2 * ,,	9	6 ,,
Obscured yellow	10	1·5 ,,	10	5 ,,
Dark	12	3 * ,,	12	14·5 ,,

The plants were removed from the bricks and allowed to dry in the air for eighteen hours. The following table shows the increase of weight which had taken place in them during their growth :—

	Original weight of 12 peas.	No. of plants which had germinated.	Weight.	Average weights of each.	Average increase of original weight.
Colourless	33 grs.	10	54 grs.	5·4 grs.	2·7 grs.
Blue	34·5 ,,	12	73 ,,	6·1 ,,	3·2 ,,
Red	30 ,,	11	47 ,,	4·3 ,,	1·8 ,,
Yellow	34 ,,	11	72 ,,	6·5 ,,	3·7 ,,
Obscured colourless	35·5 ,,	10	83 ,,	8·3 ,,	5·4 ,,
Obscured yellow ...	31·5 ,,	10	85 ,,	8·5 ,,	5·9 ,,
Dark	·31·5 ,,	12	150 ,,	12·5 ,,	9·9 ,,

* Very various.

It being thought that the disproportionate weight of the plants which had grown in the dark might be partially owing to their not having become thoroughly air-dried in eighteen hours, on account of their succulent character, they were exposed in the same manner for forty-eight hours. Their weight was then reduced to 66 grains, whilst those grown under the obscured colourless (succulent as they were) lost in the same time only 14 grains; and those under the obscured yellow appeared rather to have gained weight.

The increase in weight in these instances must be attributed, as in the case of the wheat, to the absorption of water, and it seems to be in almost reverse ratio to the healthiness of the plant; for those under the red, which had the best appearance at first, showed by far the smallest increase in weight; and those under the blue, which were afterwards better looking, had not increased greatly.

In the comparative experiment made without any glass shade, one pea began to germinate on May 23rd; this was shortly followed by two others, but only one of the three grew to any size. When measured on June 6th, its root was found to be only 0·75 inch long; its stalk had attained a length of 4·5 inches; its leaflets were deep green, appearing as healthy as, if not healthier than, any under the glass shades, and when removed from all moisture for eighteen hours, it weighed 5·5 grains, showing an increase of 2·7 grains on its original weight.

On examining these results we are led to draw the following conclusions, as far as peas are concerned, growing under the conditions of the experiment. The cutting off of the chemical rays favours the first germination of the seed, and this appears to be the principal, if not the only advantage of the darkness obtained by burying the seeds in the soil. The development of roots also requires the absence of the chemical ray, yet it does not go on to the greatest extent when all the solar influences are excluded, but is favoured rather than otherwise by heat and luminosity. The first development of the plume also proceeds best under the same circumstances; yet these are not the conditions which produce a healthy plant: if all the solar radiations be withdrawn, whether entirely or only to a great extent, the plants absorb much water and grow very tall, without developing secondary branches or many leaves. The whole force of these radiations, on the contrary, prevents or greatly impedes the growth of these plants under the circumstances of the experiment. As peas grow commonly in the full sunshine, it would be interesting to observe whether the negative result obtained arose from the absence of soil about the roots, from excessive moisture, or from some other cause. The experiment, however, affords us no data for determining this question. The chemical force is the most antagonistic to the growth of the pea, and luminosity also militates against it: the heating rays are favourable; but let the plant be fairly established, and those radiations which are comparatively speaking devoid of light, but replete with chemical power, are the most suited to the production of a healthy growth. The influences which facilitate rapid growth are diametrically opposed to healthy development. It should be borne in mind, however, that these observations relate only to a very early stage of the plant, and teach us nothing respecting the full-grown pea, or the evolution of the flower or fructification.

If we compare the effect of the various solar radiations upon the germination of wheat with the effect produced upon that of peas, we are struck with the great diversity between them. This was particularly apparent during the progress of the experiment. The colourless and the red glasses happened to stand side by side on the table, and it was curious to notice under the former glass a tall and vigorous crop of corn-plants with a mere matting of

stunted roots from the peas, while under the other a thick crop of green spreading plants arose from the germinating peas, but the wheat-plants were few, straggling, and unhealthy in appearance.   When, however, we come to look more closely into the phænomena, we see certain points of resemblance. In both cases the cutting off of the chemical ray facilitates in a marked manner the process of germination, and that both in reference to the protrusion of the radicles and the evolution of the plume.   The unnaturally tall growth of the stem, and the poor development of leaves in darkness, more or less complete, is also common to both these specimens of the monocotyledonous and dicotyledonous plant.   In both cases too, the yellow ray exerted a repellent influence upon the roots, giving the wheat a downward and the pea roots a lateral impulse.

The object of employing a partially obscured yellow glass in these experiments, was to decide if possible the question which has been asked, Does yellow light stop germination by some specific action or merely by the excess of light? Contrary to the experience of some others, who, I believe, have experimented on seeds covered with soil, and on other plants than those employed by me, the yellow light did not interfere at all with germination, in the experiments just described.   In the case of both plants, indeed, it decidedly facilitated the early development of both the root and the plume.   That the yellow ray, however, has a specific action of its own, is proved by the most cursory glance at the facts already recorded; the yellow and the obscured yellow give quite different results from those of any of the other glasses.

The diversity between the effect of the same qualities of light upon the growth of the wheat and the pea leads us to suspect at once any generalisations affecting other plants which may be drawn from the observed influence of light upon one particular plant, especially, of course, when they are of different orders.   This will account for some of the diversity of statement made by previous experimenters in these fields.

The subject may be, however, further elucidated by referring to some of these.   Dr. Draper, in his elaborate investigation of the forces which exert a controling influence on the growth of plants, records a series of experiments on peas.   He placed them just after they had begun to grow in blue, red, and yellow light, and also in the dark, and in the open air.   His observations were confined to the third and fourteenth days.   At the former period he found that under the red the plant had attained 4·5 times its original size, and had produced double the number of leaves; under the blue, three times its original height, with also double the number of leaves.   In the dark there was about the same increase of altitude, while in the open air only twice the original height had been attained, and there were no fresh leaves; and under the yellow light, a still smaller advance had been made.   On the fourteenth day he found all his pea-plants green, though varying a little in the character of the colour, except those which had been placed in the dark, which were of a pale whitish yellow, the plants vigorous, thirteen times their original height, but with no fresh leaves.   On the whole, then, as far as Dr. Draper's experiment goes, it is in accordance with my results.

M. Senebier describes an experiment performed by him on lettuce-seeds sown in little cups and placed respectively in the open air in full light of day, in darkness, and under glass vessels filled with colourless, yellow, red, and violet fluids.   "Observing then the effects produced by the different portions of light which were thus permitted to act, he found that the plants illuminated by the yellow rays grew most rapidly in height; next, those in the violet rays; afterwards those in the red rays.   The plants which grew in light transmitted through water were still smaller and approached in size to

those which flourished in the open air, while those in perfect darkness attained the greatest height of all. These last plants perished on the eighth day, and those in the yellow light on the ninth day, while all the others continued to vegetate. At the end of about five weeks, the plants growing under the red vessel were 4 inches and 9 lines in height; under the violet vessel 3 inches and 3 lines; under the water vessel 2 inches and 10 lines, and 1 inch and 3 lines in the open air. With respect to the general appearance of the plants, the leaves of those which grew in red light were smaller and less smooth than those of the plants in violet light, or than the leaves of the plants confined under water, or than the leaves of those which grew in the open air. As to colour, the leaves exposed to yellow light were at first green and afterwards became yellow; those in red light appeared green and preserved a tinge of that colour; those in violet light were quite green and their colour augmented with their age; while those raised in obscurity possessed no verdure at all." These experiments were repeated on French beans with nearly similar results, but beyond the observation that " in proportion as the plants grew in height, in different kinds of light, the number and size of their leaves diminished," his attention appears to have been directed only to the question of colour*.

Besides the experiments already detailed in this Report, and those on wheat and *Malope trifida* described in my former one, I have a few other observations on the effect of various qualities of light on the growth of plants from the seed, which it may be worth while briefly to record. They were made on the *Collinsia bicolor* of the florists, and *Mignonette*.

Seeds of the *Collinsia* were sown in garden mould in glasses, and placed under the colourless, blue, yellow, red, and darkened shades, on a table before a window which had a N.W. aspect. The perforated boards were used for supporting the glass covers. The experiment was commenced on the 6th of July in last year. On the 9th it was found that germination had taken place under each glass except the yellow, where no plant grew until the 14th. Under the colourless glass, the plants grew and flourished till the beginning of August, when they all faded and died. Under the blue and red glasses they grew well for awhile, but began to droop by the 26th of July. Those under the darkened glass existed rather longer, but they were tall and scraggy, and the leaves did not fairly open. Only three plants germinated under the yellow shade; they were all unhealthy and died before the 26th. On August 4th, seeds were sown afresh under each glass. Much the same order of growth was observed.

On October 12th, a hundred seeds of Mignonette were sown in each of seven glasses filled with garden mould. They were placed about a third of an inch below the surface. Six of the glasses were covered respectively with the colourless, blue, red, yellow, obscured colourless, and obscured yellow shades, and the seventh was placed in a dark closet. It should be observed that the closet was rather warmer than the room. The Mignonette seeds began first to germinate in the dark, then under the blue; then, after the lapse of a few days, they appeared under the red, and colourless, and the obscured colourless glasses. The yellow ray long retarded, and very nearly prevented their germination. Those in the dark were tall, thin, and yellow; they all died about November 1st; the others soon followed, excepting one plant under the colourless glass, which was found still alive with four green leaves on December 10th.

The investigations of many experimenters have shown that oxygen is

* From Ellis's " Farther Inquiries," &c.

necessary in the germination of seeds.   The explanation given is that that element is required for instituting the action that converts the fecula of the cotyledon into sugar.   It is unquestionable, that in the majority of cases, plants after the first stage of their growth require a certain supply of carbonic acid, by the decomposition of which they obtain carbon, setting free oxygen.   My brother and I have shown that plants will exist well for a considerable time in an atmosphere devoid of oxygen, for instance in nitrogen, hydrogen, coal-gas, or carbonic oxide.   In order to see the effects of all these atmospheric conditions on the germination of wheat and peas, the following experiments were made during the latter part of May and the beginning of June.

Six wheat-seeds and six peas were placed on folds of linen floating on mercury, and covered with a colourless glass jar having a capacity of about 20 cubic inches.   The linen preserved the seeds from the mercury, and was kept wet by the introduction of a small quantity of water.   The jar was full of atmospheric air, and was placed on the table before the window having a S.E. aspect.   After a couple of days or so the peas germinated, and shortly afterwards the wheat.   They grew for about a week, and retained a healthy appearance much longer.   The experiment was twice performed with similar results, and showed that the arrangement was applicable to the proposed experiments.

A precisely similar arrangement was made in a jar containing 29 cubic inches of hydrogen gas, and having in it a tube containing pyrogallate of potash, so as to absorb any trace of oxygen which might be accidentally present in the gas, or might be evolved from the seeds themselves.   In four days the swollen peas had begun to burst.   They put forth short radicles, but no plume, and in about a week afterwards they were all decaying.   The wheat showed no appearance whatever of germination.   This experiment was twice performed with the same result.

Another such arrangement was made in a jar filled with carbonic acid. Not the slightest appearance was indicated by either the wheat or the peas. They decayed, becoming soft and swollen, and emitted a most offensive smell on the removal of the jar.

The same was done in a jar filled with common air, and containing a solution of caustic potash in a small capsule, so as to remove any carbonic acid which might be given off by the seeds.   In about three days both the wheat and the peas had begun to burst; four out of the six of each continued to grow for about six days, and remained healthy afterwards.   The removal of the carbonic acid, then, did not affect the germination.   I subsequently found that in this experiment I had almost exactly repeated one of Mr. Ellis's in his 'Inquiry into the changes produced on atmospheric air by the germination of seeds,' &c.   He employed peas, and satisfied himself that all the oxygen in the jar had been absorbed by the germinating plants.

The effect of oxygen on the germination of wheat and peas under the influence of the different solar radiations was also tried.   The small coloured glasses, having a capacity of 172 to 177 cubic inches, were employed, and the experiments were conducted like those under the coloured shades which have been already detailed.   The seeds were placed on the bricks on May 2nd. On the 8th, both the wheat and the peas had burst under the colourless glass, but they soon became mouldy, and before the end of the month they were quite dead.   The seeds under the yellow glass ran much the same course ; but those under the blue glass, though they did not burst till the 11th, grew well, and by the 26th two of the wheat plants had attained a height of 4 or 5 inches.   The experiment was discontinued on June 5th.   The plants

were removed from the brick for desiccation, and on the following day the five of the wheat which had germinated were found to weigh 8 grains, giving an average of 1·6 grain for each, or an increase of 0·9 grain on the original weight. All the six peas had germinated and weighed 26 grains, giving an average of 4·3 grains for each, or an increase of 1·6 grain on the original weight.

Thus far I have proceeded in the investigation. Many interesting inquiries naturally suggest themselves; some have been already alluded to, for instance, the influence of light upon the colours of flowers; the amount of exclusion of light effected by the soil; the different condition of solar influences required by wheat or by peas at later periods of their growth; and the extension of the observations to other seeds. Other questions might be raised, such as,—What character of light promotes best the absorption of oxygen in germination? At what period in the growth of a plant does oxygen become unnecessary? Is oxygen requisite for the full development of a bulbous-rooted plant? Does carbonic acid act specifically in the prevention of germination, or merely by the exclusion of oxygen? How far does the rapid development of a plant in an early stage interfere with its healthy growth at a later period?
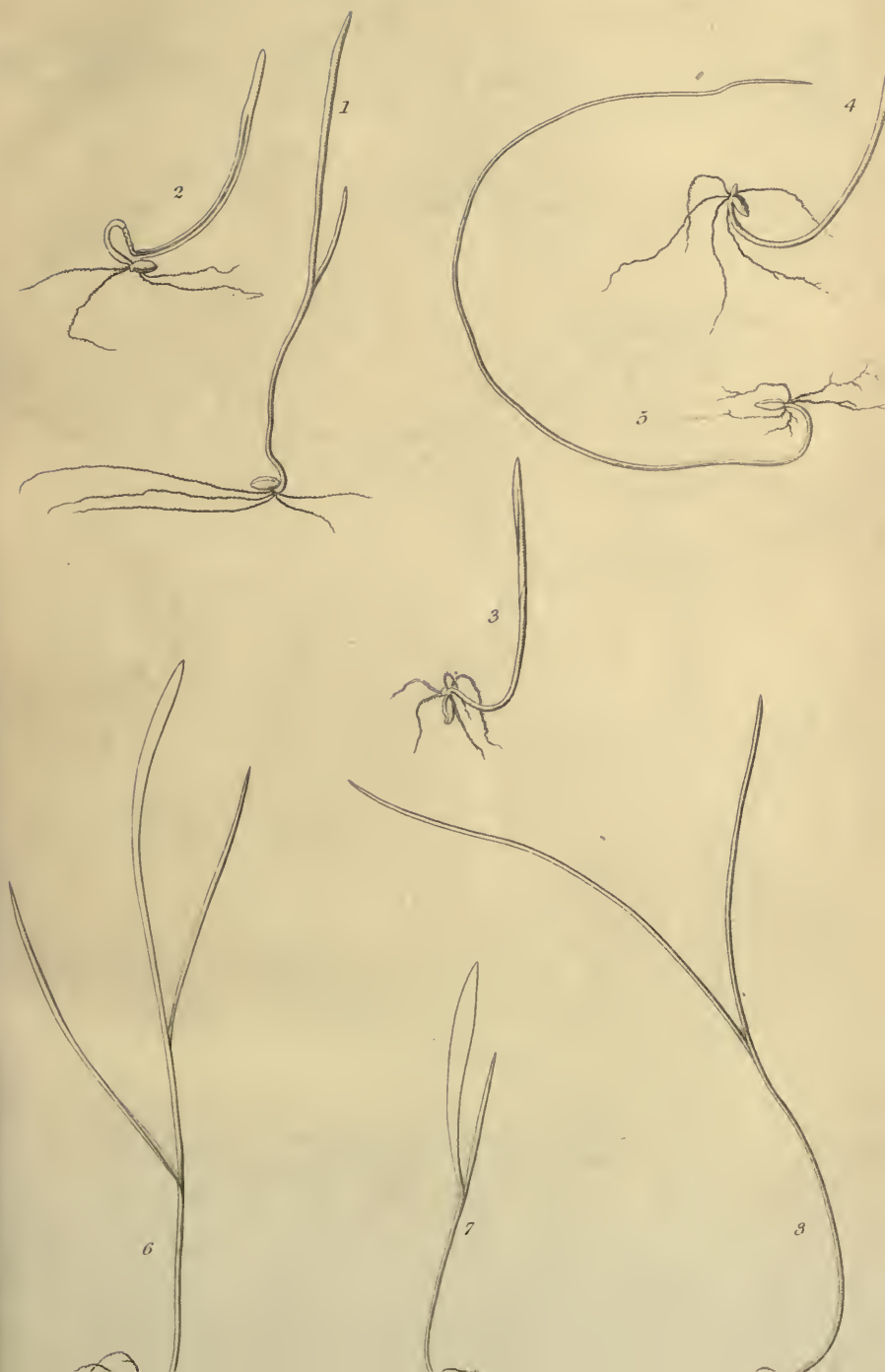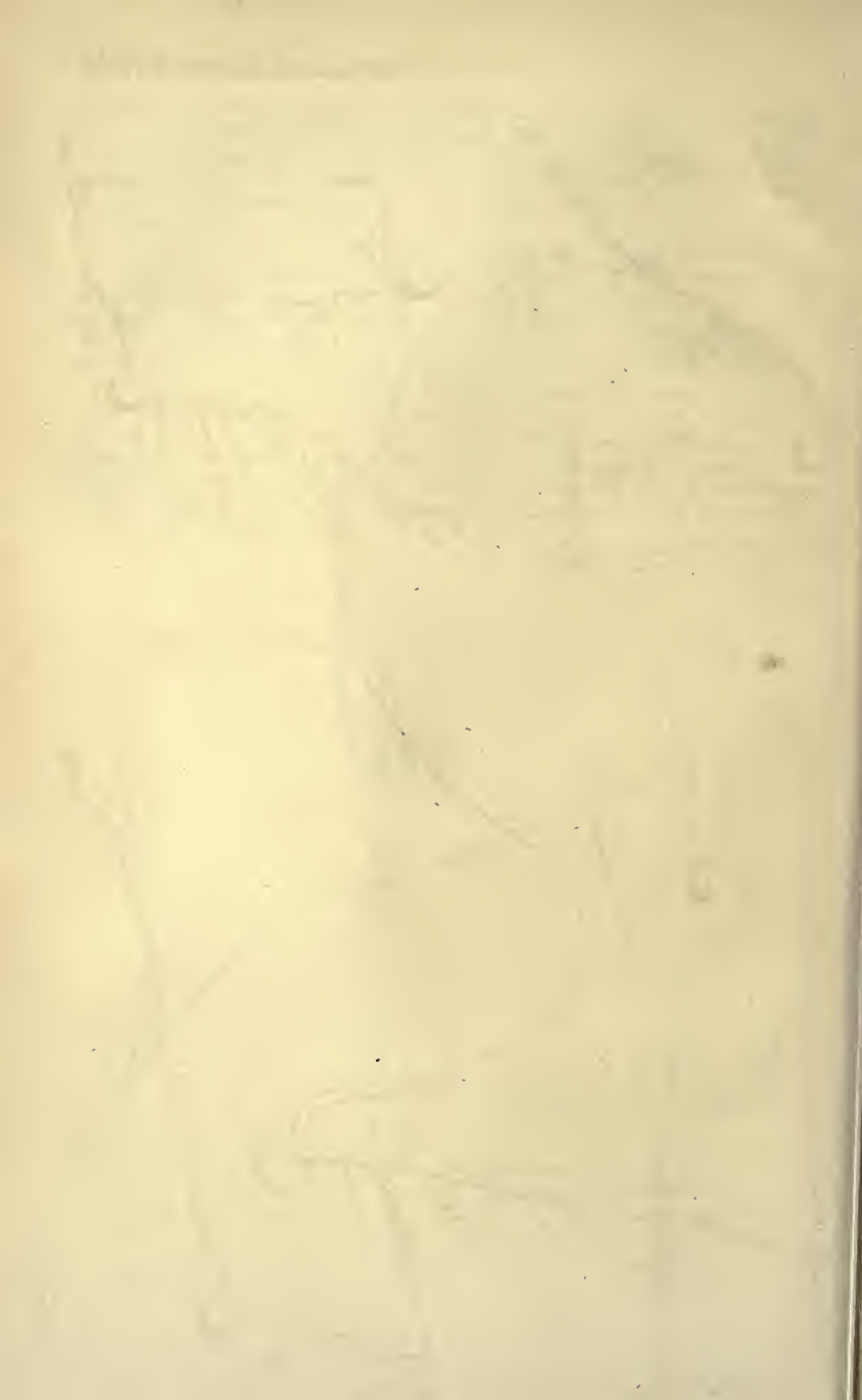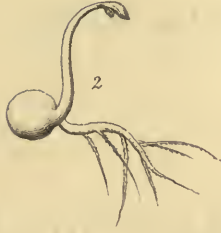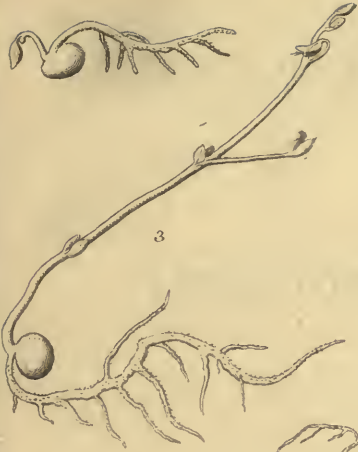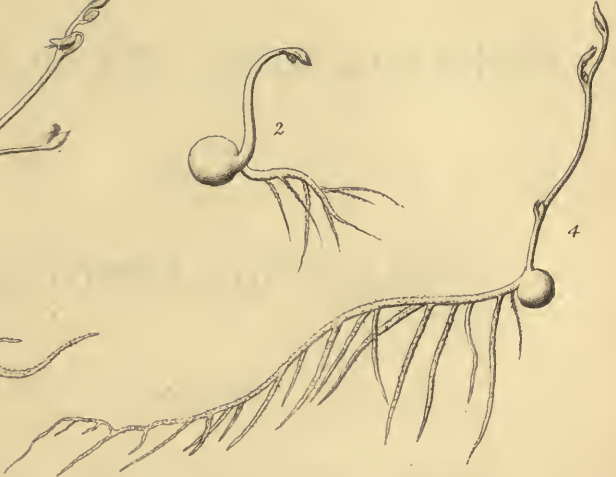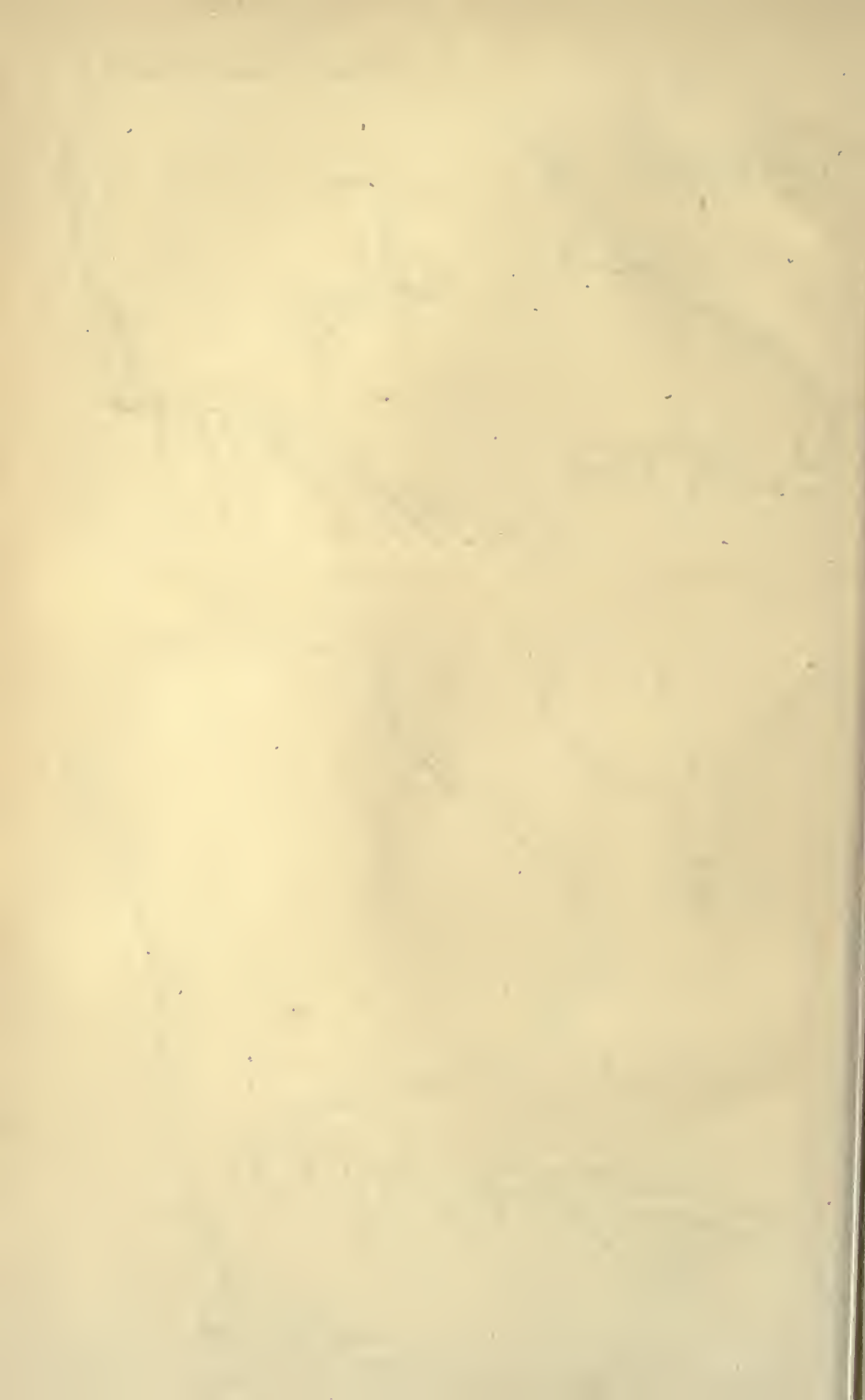
ON THE

INFLUENCE OF THE SOLAR RADIATIONS

ON THE

VITAL POWERS OF PLANTS

GROWING UNDER

DIFFERENT ATMOSPHERIC CONDITIONS.

PART III.

By J. H. GLADSTONE, Ph.D., F.R.S.

DURING the course of the experiments recorded in my last Report, a number of questions suggested themselves, and were incorporated in my remarks. To the solution of some of these I have since addressed myself.

In previously examining the germination and early growth of wheat and peas under the various coloured glasses and in obscurity, more or less complete, it was thought necessary not to cover the seeds with mould, since that would have greatly interfered with the quantity of the light that surrounded them. For certain reasons also the air was allowed to remain unchanged during the whole vegetation of the plants. A number of well-defined results were obtained; but they were liable to the objection that the wheat and peas were not grown under normal conditions. I have felt it to be the more necessary to remove this objection, seeing that one of the most important results arrived at was in direct antagonism to what other observers had remarked; the result was, that "the cutting off of the chemical ray facilitates in a marked manner the process of germination, and that both in reference to the protrusion of the radicle, and the evolution of the plume." During the spring of the present year, therefore, another series of experiments was instituted upon the growth of the same plants—wheat and peas—under the same coloured and obscured bell-glasses, with this important difference, that a little garden-mould was placed on the bricks, together with the seeds, but not in sufficient quantity to cover them from the light. The bricks were sunk in the earth of a small garden attached to my residence in London; the seeds were kept well-watered, and a slight change of air was permitted. The experiment was commenced on April 3. It was thought unnecessary in this instance to keep any record of the weather; suffice it to say, that the season was generally backward, and that cold east winds prevailed during the latter part of April, which interfered with the growth of the plants materially. Owing most probably to this circumstance, the experiments now detailed were not so successful as those of the previous year; the main results, therefore, will only be recorded.

In respect to the wheat, it began, as before, to germinate most speedily in obscurity, but of the coloured glasses the blue appeared to be the most favourable to its growth; the red light seemed also advantageous. On May 18th, when the experiment was put an end to, the best developed plants were found under the obscured colourless glass.

As to the peas, they also grew best and most rapidly in obscurity. Some circumstance militated against their proper development under the colourless and coloured glasses, with the single exception that the roots had been put forth well under the blue glass. On May 18th, it was found that in the dark all the peas experimented with had put forth long roots, and most of them had grown tall plants; while under the partially obscured colourless and partially obscured yellow glasses, all the peas had grown, giving plants, which for the most part were taller, more succulent and less healthy in colour than those which, having been planted at the same time, had grown in the garden without any covering. The peculiarly beneficial effect of the calorific ray on the growth of peas was not observed in this instance.

Notwithstanding the imperfect success of this series of experiments, they give support to the view generally entertained of the efficiency of the chemical ray in facilitating germination, which, however, my previous experiments (in accordance with those made by Dr. Daubeny) directly contradict.

The cause of this contrariety might naturally be sought for in the fact that there was soil about the seeds in this year's experiment. In hopes of determining this point, and as the season was not too far advanced, the following experiments were instituted.

Two sets of the large, colourless, blue and yellow bell-glasses were taken. The one set was placed over bricks in plates filled with water, and on the bricks were simply laid, in each instance, twelve grains of wheat and eight peas, previously weighed. They were placed in a sunny situation in the garden, and the air was occasionally changed. This set, therefore, was analogous to those described in the last Report. The other set was placed in a sunny part of the garden over spots where the same number of grains of wheat and of peas, also previously weighed, had been sown in the mould. They were watered, and the air was changed from time to time.

On May 26th, that is a few days after the commencement of the experiment, the wheat and peas had begun to burst under all the six glasses. Summer weather succeeded, warm sunshine and warm showers.

The wheat on the bricks appeared to germinate first under the blue glass, and it grew more quickly there, yet not so many had shown signs of life as under the other glasses, and in about a month's time it was found that the plants were growing about equally well under all the three shades, though somewhat impeded by the luxuriant growth of the peas. On July 19th the plants that had thriven were counted, measured, removed from the bricks, allowed to dry in the air for twenty-four hours, and then weighed.

	No. of plants.	Weight.	Average weight.	Average increase on original weight.	Average length of plants.
		grs.	grs.	grs.	inches.
Colourless	3	5·5	1·8	1·1	10
Blue	2	5·5	2·7	2	14
Yellow	4	8·5	2·1	1·4	13

The wheat that was sown in mould was found on May 30th to have grown to the height of two inches under the colourless and the yellow shades, but the plants were not so tall under the blue. Some of the wheat under the yellow was remarkably fine. On July 19th, the following were the observed results, the weight being taken as before:—

	Number of plants.	Weight.	Average weight.	Average increase in weight.	Average length of plants.
		grs.	grs.	grs.	inches.
Colourless	3	20·5	6·8	6·1	20
Blue	2	6	3	2·3	14
Yellow	4	31·5	7·9	7·2	23

It is worthy of remark, that whether with or without mould, the smallest number of wheat-seeds have germinated under the influence of the chemical ray; yet they appear to have grown well under these circumstances up to a certain point, but the plant seems to have required the luminous or the calorific rays in order to profit much by the soil.

The peas that were placed on the damp bricks were found on May 30th to have put forth radicles of half an inch or upwards in length under all the glasses,

those under the blue being somewhat the longest. Presently the effect of the yellow light in causing the production of very long roots began to show itself. All the seeds germinated. On July 19th, the peas were treated as the wheat had been.

	Number of plants.	Weight.	Average weight.	Average increase of weight.	Average length of plant.
		grs.	grs.	grs.	inches.
Colourless	8	47	5·9	1·4	6
Blue	8	21·5	2·7	—1·8	9
Yellow	8	32	4	—0·5	7·5

The peas that were sown in mould began to grow equally at first, but in about three weeks' time those under the colourless glass were the shortest. They grew luxuriantly and filled the bell-glasses, but at the beginning of July the pea-plants which grew under the blue shade, and which had never thriven, shrivelled and died away. The leaves never opened properly. The following were the numerical observations made July 19th :—

	Number of plants.	Weight.	Average weight.	Average increase of weight.	Average length of plant.
		grs.	grs.	grs.	inches.
Colourless	8	98	12·2	7·7	33
Blue	...	...	......	...	...
Yellow	4	28	7	2·5	24

On comparing these last results, it is evident that whether with or without mould, the peas that grew under the blue glass display an inferiority. The peas growing in mould certainly produced the most healthy plants when they were exposed to all the influences of the solar ray, and the deprivation of the luminous principle proved fatal to them in their more mature growth, although the removal of the chemical ray had little effect.

These experiments indicate no relative difference in the actions of the three different coloured lights upon the germination of seeds, dependent on the absence or presence of soil; and they afford further confirmation of my former view, that the chemical rays rather militate against than favour the healthy germination of at least these particular instances of Monocotyledonous and Dicotyledonous plants. I remain unacquainted with the reason why the experiments of some other observers, and indeed one or two of my own, exhibit a tendency of seeds to germinate more readily under a blue glass. It may be from the more complete darkness thus produced; but the problem is evidently a difficult and intricate one, and I abstain from further conjecture.

Among the queries at the close of the last Report was the following :— "Does carbonic acid act specifically in the prevention of germination, or merely by the exclusion of oxygen?" It was thought that this might be determined by substituting that gas for the nitrogen in the air, and observing whether seeds germinated equally well in such an atmosphere. Experiments previously recorded rendered it unnecessary for me to satisfy myself again that peas and wheat would commence growing in a colourless jar of twenty-five cubic inches capacity. Such a jar was therefore filled with a mixture of four parts of carbonic acid and one part of oxygen, placed over mercury, on

the surface of which was a little water; it was placed in the garden with a sunny aspect. Mould was introduced, and some seeds of wheat and peas. After fourteen days it was found that the peas had merely split, and were black and decomposed, while the wheat showed no signs of germination, and were quite soft and decayed. An analogous experiment was made with pure oxygen gas. Both the peas and wheat germinated and grew a little, until no doubt the atmosphere of the jar was in a great measure converted into carbonic acid, when they also decayed. It appears then that carbonic acid in considerable excess has a positively injurious effect on germination.

In concluding the record of this investigation of the influence of solar radiations on the growth of plants under different atmospheric conditions, I feel very sensible of the imperfect nature of the results, and am convinced that such are the difficulties of the inquiry, that the conclusions actually arrived at must not be generalized without the greatest caution. Yet at the same time I beg to express the hope that other observers may take up some of the questions, to which I have incidentally alluded, but which still remain unanswered.

On the Explosive Compound usually denominated Iodide of
Nitrogen.

By J. H. Gladstone, Ph.D., F.C.S.

The following experiments were made last summer with a view to settle the real composition of the so-called " iodide of nitrogen." This substance resulting from the mutual action of iodine, and ammonia in solution, has already been the subject of much investigation ; and the study of its reactions by different chemists has led to four different formulæ being assigned to it. The extremely explosive character of the substance precludes the idea of analysing it in the usual manner, as it would be impossible to place a portion in the scale-pan of a balance with any safety after it had been dried. Indirect modes of analysis, by which the relative proportion of its constituent elements is determined, appear to be offered by various decompositions, which the black powder may be made to undergo. M. Bineau* alone, has studied any of these hitherto : and his experiments led him to assign to the so-called iodide of nitrogen the composition NHI_2. The quantitative results recorded below will test the truth of this formula.

The substance employed by me was always prepared by decomposing an alcoholic solution of iodine by means of ammonia in excess. The black powder thus formed was completely washed by suffusion with distilled water, and decantation. It was found, that during this reaction, an amount of iodide of ammonium is formed slightly exceeding half the amount of iodine employed : a mere trace of iodic

* Ann. Ch. Phys. [3] XV, 71.

acid is also produced. This fact is opposed to the formula NI assigned to the black powder by Mitscherlich ; for

$$4\ NH_3 + 4\ I = NI + 3\ NH_4\ I\ ;$$
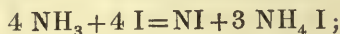
in which case the iodide of ammonium obtained would be quite three-fourths of the iodine originally acted upon ; but it decides nothing, as to whether 1, 2, or 3 atoms of hydrogen in the ammonia are substituted by iodine ; for

$$2\ I + 2\ NH_3 = \quad NH_4\ I + NH_2\ I \quad \text{(Millon)}.$$
$$4\ I + 3\ NH_3 = 2\ NH_4\ I + NHI_2 \quad \text{(Bineau)}.$$
$$6\ I + 4\ NH_3 = 3\ NH_4\ I + NI_3.$$
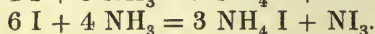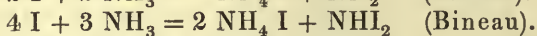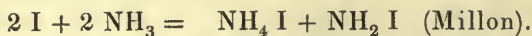
The black powder suffers spontaneous decomposition in pure water. Bubbles of gas are slowly given off ; iodine is set free ; and the solution (which is acid to test paper) contains hydriodic and iodic acids, together with ammonia. In an attempt to make use of this decomposition as a means of analysis, the iodic acid was found to be to the hydriodic acid in the ratio of 1 atom to 8·44 atoms ; but it is not likely that the two acids always maintain the same proportion.

The addition of ammonia to the water in which the black powder is immersed, tends to prevent its spontaneous decomposition. Potash, on the contrary, accelerates it. So do acids in general. A solution of carbonate of potash has much the same action as pure water.

Chlorine destroys the black powder, but not instantaneously ; bromine water causes its immediate decomposition. Strong nitric acid attacks it violently.

Hydrosulphuric acid causes its instant decomposition without the evolution of any gas, and with the formation of ammonia and hydriodic acid alone, sulphur being in the meantime deposited. This affords a ready method of determining the relative proportion of iodine and nitrogen. Accordingly, some of the black powder was diffused through water, and a stream of hydrosulphuric acid gas was passed through it, until the solution, which assumed at first a red tint, became colourless and smelt strongly of the gas. It was then gently heated and filtered ; the hydriodic acid was precipitated as silver-salt, excess of silver was removed by the addition of a large excess of hydrochloric acid, and the resulting chloride of ammonium was estimated in the usual manner. The amount of ammonio-chloride of platinum obtained was 5·83 grs. ; that of iodide of silver 12·53 grs., which is equivalent to

Nitrogen . . . . . 0·366 grs.
Iodine . . . . . 6·75 „

If we divide these numbers by the atomic weights of the respective elements, we obtain :

Nitrogen 261
Iodine. 533

or the proportion of 1 atom of nitrogen to 2·04 atoms of iodine.

The action of sulphurous acid appeared to offer the means of determining the relative proportion of nitrogen, iodine, and hydrogen also, if that element really be a constituent of the black powder. The transformation of the substance into ammonia and hydriodic acid takes place instantly, without the evolution of any gas, unless the temperature be suffered to rise considerably, when a secondary action is instituted. At the same time, a quantity of sulphurous acid is converted into sulphuric acid, equivalent of course to the quantity of water decomposed, in order to supply the necessary hydrogen. A carefully prepared fresh solution of sulphurous acid was added gradually to some of the black powder diffused through water, until the decomposition was complete. The solution thus obtained was divided into two equal portions. The one portion was evaporated down with excess of hydrochloric acid, and the ammonia was converted into platinum-salt ; the other portion was very gently warmed to expel sulphurous acid, nitrate of silver was added to precipitate the iodine, and subsequently the sulphuric acid was thrown down as baryta-salt. There were obtained 8·65 grs. of ammonia-chloride of platinum ; 18·53 grs. of iodide of silver ; and 17·57 grs. of sulphate of baryta. This is equivalent to

Nitrogen . . . . . . 0·542 grs.
Iodide . . . . . . 9·98 „
Sulphuric acid . . . . 6·04 „

Dividing these numbers by the atomic weights, we obtain :

Nitrogen . . . . . 388 or 1 equiv.
Iodine . . . . . . 788 „ 2·03 „
Sulphuric acid . . . 1520 „ 3·92 „

This confirms the preceding result, and shows, moreover, that the black powder contains 1 equivalent of hydrogen ; for 1 atom of ammonia, 2 atoms of iodine, and 4 atoms of sulphuric acid, can

only arise from 4 atoms of sulphurous acid, 4 atoms of water, and NHI_2.

$$NHI_2 + 4 SO_2 + 4 HO = NH_3 + 2 HI + 4 SO_3.$$
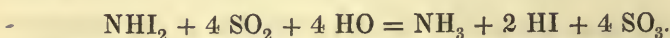
Serullas* observed, that when this black powder is decomposed by dilute hydrochloric acid, a red solution is obtained, from which the addition of an alkali reprecipitates the explosive compound, a portion, however, being always decomposed into its elements. Millon† made the further observation, that if the black powder be treated with a saturated solution of hydrochloric acid, it disappears without the evolution of any gas, and the resulting solution is neutral to test paper. He believes that the substance is resolved into ammonia and the acids of iodine, and concludes from this peculiar reaction that the explosive body must have the composition $NH_2 I$. It is difficult to see how this conclusion follows from the premises: the more natural idea would be, that the black powder, being ammonia in which a portion of the hydrogen is replaced by iodine, combines as such with the hydrochloric acid, thereby neutralising it. Yet Serullas has long since recorded various reasons tending to prove that this is not the case: he believed that the solution contained iodic and hydriodic acids, along with the hydrochloric acid; and what confirmed him in this belief, was the observation, that when these two acids of iodine are mixed together, and supersaturated with ammonia, the explosive compound is obtained, especially if hydrochloric acid be present. Now, this certainly arises from the two acids, when mixed, reacting upon one another to produce free iodine; and the explanation of the eminent chemist just mentioned does not account for the fact, that, when the decomposition of the black powder has been effected by water, or other acids than the hydrochloric, a solution is obtained, from which ammonia does not reprecipitate it.

On repeating the experiment, I found that the red solution obtained by dissolving the explosive compound in strong hydrochloric acid, contains not a trace of free iodine; it gives no blue colour with starch. When evaporated to dryness in a water-bath, it comes out as a solid body of a somewhat yellow colour, soluble in water or alcohol, and neutral, or nearly so, to test paper. If potash or baryta-water be added to this solution, it re-precipitates the black powder. The addition of nitrate of silver causes a mixed precipitate of chloride and iodide of silver. Sulphurous acid gives rise to a

separation of iodine, which a larger quantity converts into hydriodic acid. The dried substance, when heated *per se,* suffers decomposition; it gives off a pungent odour, then iodine sublimes, and afterwards chloride of ammonium. Ether extracts from the evaporated solution that which imparts to it its colour, and leaves some chloride of ammonium behind. All these reactions are perfectly explained by considering the solution produced by means of hydrochloric acid, as a mixture of chloride of ammonium and protochloride of iodine. The reaction is as follows:

$$NHI_2 + 3\ HCl = NH_4\ Cl + 2\ ICl.$$
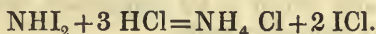
And it has been already ascertained by Mitscherlich that the explosive compound is produced when protochloride of iodine is treated with ammonia. The reaction in this case will be:

$$2\ ICl + 3\ NH_3 = NHI_2 + 2\ NH_4\ Cl.$$
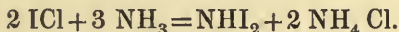
The same chemist states that terchloride of iodine with ammonia causes the formation of the same black powder. If this be really the case, we must suppose that some one of the oxygen-compounds of chlorine is formed at the same time. But an aqueous solution of terchloride of iodine is, to say the least, of very uncertain constitution; and even the liquid resulting from the action of *aqua regia* upon iodine may contain the protochloride. If iodic acid be dissolved by strong hydrochloric acid in the cold, a yellow solution is obtained having a chlorous odour; but I find that the addition of ammonia causes no black precipitate in such a solution, unless it has been previously heated.

In accordance with the practice now adopted in naming those compounds, in which two equivalents of hydrogen in ammonia are replaced by two of another body, this explosive compound should bear the appellation "Iodimide."

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When this paper was read before the Society, Dr. Playfair remarked, that some time since he had prepared the same explosive powder by pouring a solution of hypochlorite of lime into a solution of iodide of ammonium. He believed they were in the proportion of single equivalents; and as this reaction may be readily explained under the supposition that the compound is $NH_2\ I$, it had confirmed in his mind the view propounded by Millon. Upon considering the reaction subsequently, I perceived that a compound, having

Bineau's formula, might equally be obtained from the same salts in the same proportions, but that ammonia would appear among the products of decomposition. The reaction might be either

$$CaO, ClO + NH_4 I = NH_2 I + 2 Ca Cl + 4 HO$$
or $$2(CaO, ClO) + 2 NH_4 I = NH I_2 + 2 Ca Cl + 4 HO + NH_3$$
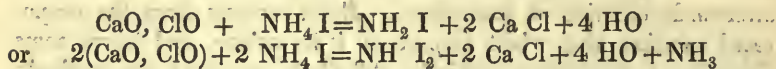
Upon repeating the experiment with bleaching powder, any alkaline reaction of which had been more than neutralized by acetic acid, I found a large quantity of ammonia set free. This reaction then, like every other with which I am acquainted, indicates the same composition for this explosive powder.
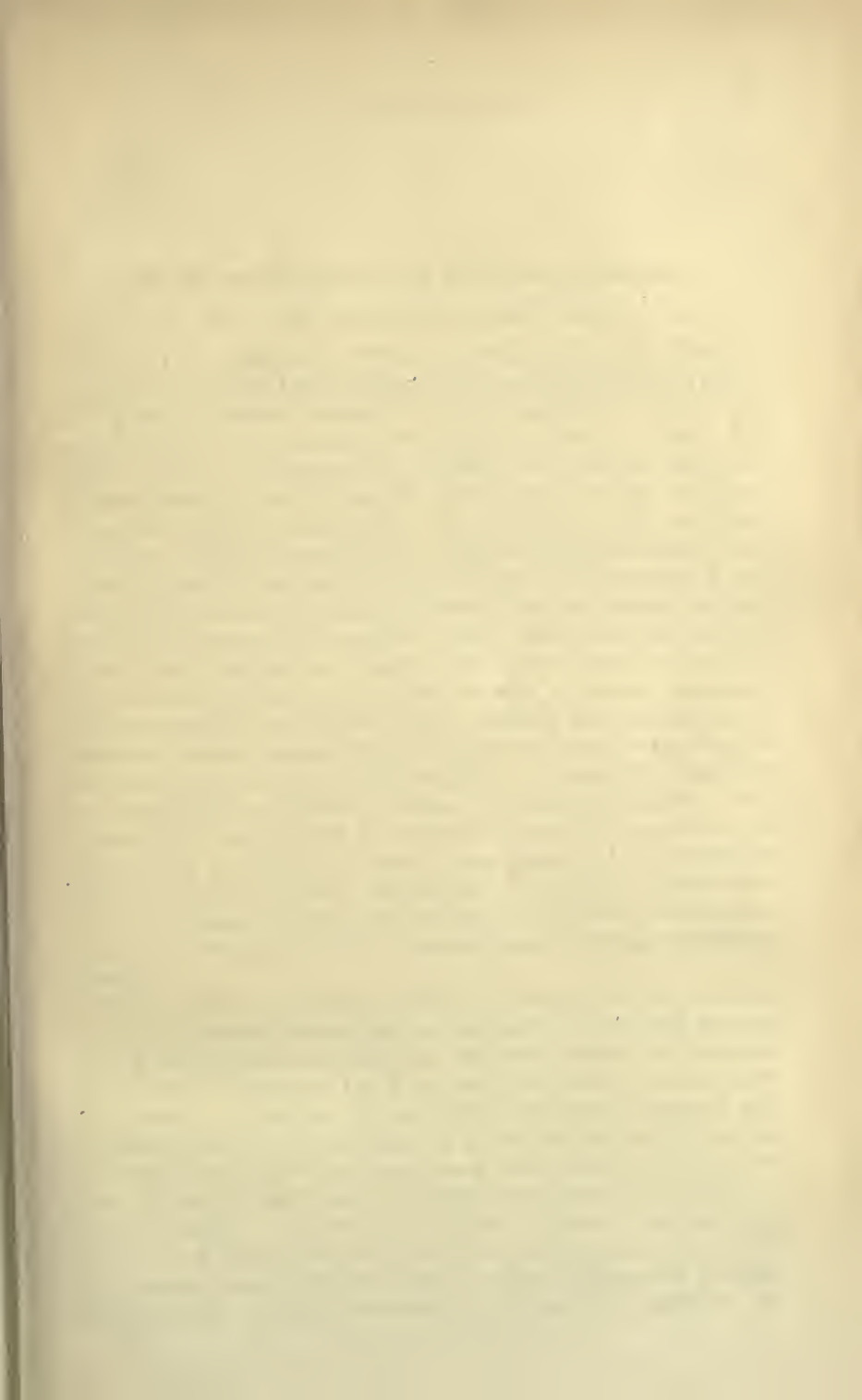
On the so-called Iodide and Chloride of Nitrogen.

By J. H. Gladstone, Ph.D. F.R.S.

On the 17th of February, 1851, I communicated to the Chemical Society a paper on the Explosive Compound usually denominated Iodide of Nitrogen, in which I assigned to it the composition NHI_2. The paper was printed in the following "Quarterly Journal." In the "Annalen der Chem. und Pharm." for October, 1852, Bunsen published an investigation of the composition of the same substance, in which he ascribes to it the formulæ $NH_3 + NI_3$, and $NH_3 + 4NI_3$, according to different modes of preparation. At first sight, there would seem an irreconcilable discordance between the results of his analyses and mine; but on closer examination this disappears, for both the methods by which he prepared the explosive powder differ from that adopted by me. He, forming the substance from iodine and ammonia dissolved in absolute alcohol, and never suffering it to come in contact with water, finds it to be $NH_3 + NI_3$; forming it by precipitating a solution of iodine in *aqua-regia* by aqueous ammonia, and washing it with water, he finds it to be $NH_3 + 4NI_3$. I, forming the substance by precipitating an alcoholic solution of iodine by ammonia, and washing with water, found it to be NHI_2, which is equivalent to $NH_3 + 2NI_3$ on Bunsen's mode of expression, and is intermediate between his two formulæ. Nevertheless I thought it desirable to repeat my former analysis, and to add some further observations towards the completion of the chemical history of this remarkable substance.

Bunsen does not adopt my method of analysis, but takes advantage of the reaction between hydrochloric acid and the black powder, which is fully explained towards the close of my paper. As, however, my method by sulphurous acid gives very exact results, I had recourse to it again. A portion of the explosive substance prepared and washed as before, and decomposed by a fresh solution of sulphurous acid, was divided into two equal parts, and yielded 0·632 grm. of iodide of silver, 0·620 grm. of sulphate of baryta, and 0·124 grm. of platinum derived from the ammonia-salt. Traces of nitrogen gas were given off during the destruction of the black powder, the amount of which was estimated at 0·04 cub. in. Half of this would be equal to 0·0004 grm. weight of nitrogen, which must be added to the

amount found to have been converted into ammonia.   The numbers given above indicate:

$$\begin{array}{lll}
\text{Nitrogen} & . & . & . & 0{\cdot}0182 \text{ grm.} \\
\text{Iodine} & . & . & . & 0{\cdot}3404 \quad ,, \\
\text{Sulphuric acid} & . & . & 0{\cdot}2131 \quad ,,
\end{array}$$

which, divided by the atomic weights, give:

$$\begin{array}{lll}
\text{Nitrogen} & . & . & 130 \text{ or } 1 \quad \text{equiv.} \\
\text{Iodine} & . & . & 268 \text{ or } 2{\cdot}06 \quad ,, \\
\text{Sulphuric acid} & . & 533 \text{ or } 4{\cdot}10 \quad ,,
\end{array}$$

This, indicating the proportion of iodine to nitrogen as 2 : 1, agrees perfectly with the result of the analyses recorded in my previous paper.

In another experiment, similarly conducted, there were obtained 0·441 grm. of iodide of silver and 0·281 grm. of ammonio-chloride of platinum.   The same amount of nitrogen gas may be reckoned as having been evolved during the action of the sulphurous acid.   These numbers indicate:

$$\begin{array}{lll}
\text{Nitrogen} & . & . & . & 0{\cdot}0142 \text{ grm.} \\
\text{Iodine} & . & . & . & 0{\cdot}2375 \quad ,,
\end{array}$$

which, divided by the atomic weights, give:

$$\begin{array}{lll}
\text{Nitrogen} & . & . & 101 \text{ or } 1 \quad \text{equiv.} \\
\text{Iodine} & . & . & 187 \text{ or } 1{\cdot}85 \quad ,,
\end{array}$$

This analysis, though it indicates rather too small a quantity of iodine, does not differ materially from the preceding.

My former view of the composition of the explosive powder prepared by precipitating an alcoholic solution of iodine by ammonia, and washing with water, is therefore confirmed.   The question remains, whether the substance is to be considered one atom of ammonia, in which two of the equivalents of hydrogen are replaced by iodine—in fact, iodimide; or whether it is to be viewed, in accordance with Bunsen's formulæ, as ammonia combined with two equivalents of teriodide of nitrogen?   Now a body of the composition assigned by the German chemist to his explosive powder, $NH_3 + NI_3$, might be equally well expressed as a compound of my NHI_2 with NH_2I:

$$NH_3 + NI_3 = N_2H_3I_3 = NHI_2 + NH_2I,$$
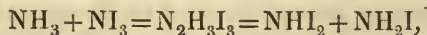
Both NI_3 and NH_2I are alike hypothetical substances; yet it appeared

very possible that the action of water on the compound might throw
some light upon the subject. It was found that when the black
powder formed in the presence of water was washed for a great length
of time, the washings still continued alkaline to test-paper. Black
powder which had been produced by mixing solutions of iodine and
ammonia in alcohol of sp. gr. 814, and had been well washed
with the same alcohol, gave, on the addition of water, a solution
which was distinctly alkaline and of a slight red tint. This colour
was removed by the very least addition of sulphurous acid solution.
Precisely the same was observed when the explosive powder was
prepared by means of absolute alcohol. A quantitative estimation
was made of the washings by water of the substance precipitated in
alcohol of sp. gr. 814. Water had been passed through it on a filter
for thirty minutes. The slightly red solution was decolorized by a
drop of sulphurous acid; it was divided into two equal parts, from
one of which 0·047 grm. of iodide of silver was obtained, and from
the other 0·028 grm. of platinum derived from the ammonio-chloride.
These numbers indicate :

Nitrogen	.	.	0·0040 grm.
Iodine	.	.	0·0253 ,,

which, divided by the atomic weights, give :

Nitrogen	.	. 28 or 1	equiv.
Iodine	.	. 20 or 0·71	,,

Hence, there must have been free ammonia as well as iodide of
ammonium, a result rather favouring the view taken by Bunsen.

The above-mentioned specimen of explosive iodide prepared by
means of alcohol, sp. gr. 814, was analysed by sulphurous acid, as in
the preceding instances. The amount of nitrogen gas given off was
too inconsiderable to be taken account of. The weights of the preci-
pitates obtained were 0·256 grm. of ammonio-chloride of platinum,
0·630 grm. of iodide of silver, and 0·649 grm. of sulphate of baryta,
which indicate :

Nitrogen	.	.	0·0162 grm.
Iodine	.	.	0·3394 ,,
Sulphuric acid	.	.	0·2230 ,,

These quantities, added to those previously found, dissolved in water,
are :

Nitrogen	.	.	0·0202 grm.
Iodine	.	.	0·3647 ,,
Sulphuric acid	.	.	0·2230 ,,

which, when divided by the atomic weights, give :

$$
\begin{aligned}
&\text{Nitrogen} && . && . && 144 \text{ or } 1 && \text{equiv.} \\
&\text{Iodine} && . && . && 286 \text{ or } 1 \cdot 98 && \text{,,} \\
&\text{Sulphuric acid} && . && 557 \text{ or } 3 \cdot 86 && \text{,,}.
\end{aligned}
$$

This result perfectly coincides with the previous analyses. The composition of this specimen of explosive powder was also NHI_2.

The unexpected confirmation of my previous views afforded by this experiment induced me to analyse a sample of the black precipitate thrown down by mixing solutions of iodine and of ammonia* in absolute alcohol. The experiment was conducted with great care, to prevent the hydration of the alcohol in any possible way during the course of it. The black powder obtained had precisely the same physical appearance as the specimens previously examined. It was decomposed and analysed in the usual manner. The amount of nitrogen gas evolved was 0·06 cub. in., half of which would weigh 0·0006 grm. The weights of the precipitates obtained were 0·253 grm. of ammonio-chloride of platinum, 0·539 grm. of iodide of silver, and 0·498 grm. of sulphate of baryta, which indicate :

$$
\begin{aligned}
&\text{Nitrogen} && . && . && . && 0 \cdot 0166 \text{ grm.} \\
&\text{Iodine} && . && . && . && 0 \cdot 2903 && \text{,,} \\
&\text{Sulphuric acid} && . && . && 0 \cdot 1711 && \text{,,}
\end{aligned}
$$

These numbers, divided by the atomic weights, gave :

$$
\begin{aligned}
&\text{Nitrogen} && . && . && 118 \text{ or } 1 && \text{equiv.} \\
&\text{Iodine} && . && . && 228 \text{ or } 1 \cdot 93 && \text{,,} \\
&\text{Sulphuric acid} && . && 428 \text{ or } 3 \cdot 63 && \text{,,}
\end{aligned}
$$

But these proportions approximate those of all my previous analyses. It is easily conceivable that different proportions of hydrogen should be replaced in different specimens, but by what variation of circumstances I obtained the substance NHI_2, instead of that analysed by Bunsen, I know not. I can but record the result of my experiment.

When the black powder is formed in the presence of water, half,

---

* Before the ammonia is dissolved in the absolute alcohol, it is necessary that it be dried. The desiccation of this gas is, I believe, usually effected by passing it over pieces or sticks of hydrate of potash; but I adopted another process. It was made to pass through a wash-bottle containing absolute alcohol, into which some pieces of potassium had been thrown. Thus was secured the advantage of the gas bubbling through a liquid, and that liquid a most hygroscopic solution of ethylate of potash perfectly free from water. Of course this process is only applicable for the desiccation of ammonia, in cases where the vapour of alcohol does not interfere.

or very nearly half the iodine employed is obtained in the solid com-
pound, and the solution becomes colourless, or nearly so, the reaction
being :

$$4I + 3NH_3 = NHI_2 + 2NH_4I,$$
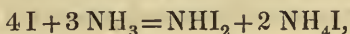
but when the iodine and ammonia are brought together in solution in
strong alcohol, a far smaller proportion of the black powder is
obtained, and the liquid remains deep-red in colour, although the
ammonia be added in large excess.   A considerable amount of
sulphurous acid solution also is required to effect its decolorization.
The addition of water causes a black precipitate, which however being
in a very finely-divided condition, is speedily acted upon by the
water, and decomposed with evolution of gas—doubtless nitrogen.
It is evident, therefore, that although iodide of ammonium is soluble
in alcohol, some other compound must be here formed.   The ratio
between the iodine in solution and that in the precipitate, was thrice
determined; as also the ratio between the hydriodic acid and the
sulphuric acid formed upon decomposing the red liquid by sulphurous
acid.   In the first experiment, alcohol of sp. gr. 814 was employed ;
in the second and third, absolute alcohol was made use of.   The
results were :

	Exp. I.	Exp. II.	Exp. III.
Iodide of silver from black powder	1·220 grm.	0·898 grm.	0·539 grm.
,, ,, ,, red solution	3·255 ,,	3·595 ,,	4·376 ,,
Sulph. of baryta ,, ,,	0·950 ,,	1·061 ,,	1·543 ,,

The proportion between the two estimations of iodine in these
three experiments is widely different, namely :

	Exp. I.	Exp. II.	Exp. III.
From black powder	1	1	1
From red solution	2·67	4·00	8·12

The ratio between the iodine and the sulphuric acid formed from
the red solution, agrees more closely, namely :

	Exp. I.	Exp. II.	Exp. III.
Iodine	1 equiv.	1 equiv.	1 equiv.
Sulphuric acid	0·59 ,,	0·60 ,,	0·71 ,,

The smaller proportion of sulphuric acid would appear to indicate
that the iodine exists in the red solution to a considerable extent in
the form of iodide of ammonium ; but it must be mixed or combined
with a larger amount of the element in some other condition.

In the third experiment, the ammonia in the red solution was also
determined. The liquid was warmed, to expel the excess of the

volatile alkali, in fact, till there was a distinct odour of iodine. It was then divided into two equal parts, and proceeded with as before. The amount of ammonio-chloride of platinum obtained was 0·723 grm.; that of iodide of silver, as before stated, was 4·376 grms.

These numbers indicate:

Nitrogen	.	.	.	0·0459 grm.
Iodine	.	.	.	2·3572 „

which, divided by the atomic weights, give:

Nitrogen	.	.	328 or 1	equiv.
Iodine	.	.	1856 or 5·66	„

There is here a remarkably small amount of ammonia indicated; probably the compound first formed in the red solution is decomposed by a slight heat, the iodide remaining in the liquid, and the ammonia volatilizing.

CHLORIDE OF NITROGEN.

It appeared highly probable that the same methods which had proved applicable to the analysis of the so-called iodide might be effective also when tried with the chloride of nitrogen. The systematic analysis of this oily liquid indeed has never been attempted excepting by Bineau. In the same memoir in which that chemist attributed the correct composition to the iodide, he assigned to the chloride the composition $N Cl_3$.* Since, however, his determinations are far from being exact, doubt might still be entertained as to the actual proportion of the nitrogen and chlorine, and whether the explosive liquid might not, like the iodide, retain some portion of hydrogen. At any rate it would be interesting to try whether the view of Bineau would be confirmed by further experiments, and how far the formula of this substance might throw light upon the rational composition of the iodide.

The so-called chloride of nitrogen was prepared in the usual way, by the mutual action of chlorine and chloride of ammonium. For each separate analysis a globule was collected of just sufficient size; and it was washed by a stream of water until the washings gave no appreciable precipitate with a silver salt. Methods similar to those employed for the decomposition of the iodide were made use of in this case also. A stream of hydrosulphuric acid was passed for a long time through water at the bottom of which was a globule of the explosive liquid. Decomposition took place slowly, sulphur

* Ann. Chim. Phys. [3], XV, 71.

being liberated, and ammonia and hydrochloric acid formed: but at the same time the usual action of water on the compound was proceeding, and thus a little nitrogen gas was produced. This was scarcely more than a trace, but not having been collected, it must have vitiated the experiments to some extent. The solution obtained after this reaction was warmed to expel the excess of hydrosulphuric acid, and filtered from the deposited sulphur. In the first experiment recorded below, the ammonia and hydrochloric acid were determined from the same portion, acetate of silver having been employed to precipitate the latter, excess of silver being subsequently removed by the addition of hydrochloric acid, and the ammonia converted into platinum salt. In the second and third experiments, the solution was divided into two equal parts, from one of which the hydrochloric acid, and from the other of which the ammonia were estimated in the usual manner.

The following are the results:

	Exp. I.	Exp. II.	Exp. III.
Ammonio-chloride of platinum	0·149 grm.	0·082 grm.	0·254 grm.
Chloride of silver	0·226 ,,	0·138 ,,	0·510 ,,

which are equivalent to:

	Exp. I.	Exp. II.	Exp. III.
Nitrogen	0·0092 grm.	0·0052 grm.	0·0161 grm.
Chlorine	0·0544 ,,	0·0340 ,,	0·1257 ,,

These numbers are in the ratio of:

	Exp. I.	Exp. II.	Exp. III.
Nitrogen	1 equiv.	1 equiv.	1 equiv.
Chlorine	2·31 ,,	2·58 ,,	3·08 ,,

The last of these estimations accords with Bineau's formula, but the average of them certainly does not, especially when it is borne in mind that, from the loss of nitrogen in the gaseous form, the chlorine will be overestimated; and thus the smallest proportion of chlorine is probably the truest.

The action of hydrosulphuric acid being evidently not calculated to give an exact means of analysis, sulphurous acid was had recourse to. It was found that a solution of that substance in water acted slowly upon the explosive compound, giving rise to ammonia and hydrochloric acid, with formation of sulphuric acid; a little nitrogen gas was evolved at the same time, but not a trace of nitric acid was formed, as is usually the case when the chloride is left in contact with water. For the purpose of analysis, a globule of the liquid was placed in a

small basin, containing a freshly prepared aqueous solution of sulphurous acid, and over it was placed a glass tube also filled with the solution in such a manner that the bubbles of gas all rose into it. After a few hours, the globule had disappeared, a certain amount of nitrogen gas was found, and its volume measured. The solution was warmed to expel the remaining sulphurous acid, and divided into two equal parts, from one of which the hydrochloric acid, and from the other the ammonia, were estimated in the usual way. The experiment was performed twice, and the following were the results:

	Exp. I.	Exp. II.
Nitrogen gas (divided by 2)	0·04 cub. in.	0·14 cub. in.
Ammonio-chloride of platinum	0·207 grm.	0·122 grm.
Chloride of silver	0·365 ,,	0·281 ,,
Sulphate of baryta	0·634 ,,	0 428 ,,

which are equivalent to:

	Exp. I.	Exp. II.
Nitrogen	0·0139 grm.	0·0105 grm.
Chlorine	0·0900 ,,	0·0692 ,,
Sulphuric acid	0·217 ,,	0·147 ,,

These numbers are in the ratio of:

	Exp. I.	Exp. II.
Nitrogen	1 equiv.	1 equiv.
Chlorine	2·56 ,,	2·60 ,,
Sulphuric acid	5·47 ,,	4·89 ,,

The results of these two experiments almost coincide,* in the proportion of chlorine and nitrogen, and they agree with the average of the experiments by means of hydrosulphuric acid. The proportion between the nitrogen and chlorine is evidently as $1 : 2·5$; and as there are 5 equivalents of sulphuric acid formed, it shows that 2·5 equivalents of hydrogen have also been supplied for the production of ammonia. The composition of the explosive chloride therefore is not so simple as that of the so-called iodide: it may be expressed either as a double equivalent of ammonia in which 5 atoms of hydrogen are replaced by iodine, viz., N_2HCl_5; or as $NHCl_2 + NCl_3$.

* There appears a considerable discrepancy between the two estimations of sulphuric acid; but it should be remembered that in such experiments as these, where a solution of sulphurous acid has been exposed for hours to the air, an excess of sulphuric acid may be expected; while on the contrary, the evolution of nitrogen in the gaseous condition, will cause less sulphuric acid to be formed. Hence, no doubt, the deficiency in the second experiment, contrasting so with the excess in the first, where much less gas was produced.

On the Compounds of Cotton with the Alkalies.

By J. H. Gladstone, Ph. D.

The beautiful effects produced by Mr. Mercer through treating cotton with a cold solution of caustic soda, are well known not only to the scientific world, but, through the medium of the Great Exhibition, to the public in general. Yet I believe the chemical compound tself has not hitherto been investigated.

This gentleman found that when cotton, or a cotton fabric is immersed in a very strong alkaline ley in the cold, a certain combination is effected. This " sodaed" cotton parts with all its alkali when washed with pure water, and the " mercerized" cotton thus produced, is not only much contracted, so that coarse fabrics have assumed the appearance of fine ones, but when dyed it displays colours of more than ordinary brilliancy.

It is evident that, by the process described above, the combination of soda and lignine is not obtained in a state fit for analysis. As the fabric issues from the alkaline ley, there adheres to it an excess of soda, and the moment it is touched by water its integrity is destroyed. It became a desideratum then to find a solvent capable of removing the uncombined alkali whilst it left the compound unimpaired. Alcohol suggested itself to my mind as likely to possess the requisite quality, especially as it might be employed in an anhydrous condition.

As preliminary experiments, two portions of pure cotton were taken, each weighing 20 grs. when thoroughly dried. The one was steeped in cold caustic soda, so dilute as not to produce Mr. Mercer's reaction, the other in a strong solution of soda. They were both soaked repeatedly in successive portions of absolute alcohol, and subsequently dried in vacuo over sulphuric acid. In Exp. I. the cotton proved to be of the original weight, and did not retain any soda; in Exp. II. the cotton had increased to 24·4 grs., and contained an amount of soda, which, when dissolved out by water, neutralized by sulphuric acid, and evaporated in a platinum dish (excess of sulphuric acid in combination being removed as usual by small pieces of carbonate of ammonia), gave 4·8 grs. of sulphate $=$ 2·1 grs. of absolute soda. From the first experiment, the conclusion may be drawn that absolute alcohol is capable of removing from cotton any portions of uncombined soda; and from the second it may be inferred that such alcohol does not decompose the compound of soda and cotton.

Having thus obtained a method, I performed a series of more exact experiments. A solution of soda of sp. gr. 1124 was found capable of combining with cotton, though it did not produce much shrinking. It was made use of in preference to a stronger solution, as it left less alkali adhering to the fibre to be afterwards washed out with alcohol.

Exp. III. 20 grs. of cotton steeped for an hour in the alkaline ley, washed repeatedly with absolute alcohol, and thoroughly dried in vacuo, had increased to 21·97 grs., and furnished 2·70 grs. of sulphate of soda.

Exp. IV. The cotton regained from Exp. II., similarly treated, showed an increase in weight to 21·09 grs., and yielded 2·71 grs. of sulphate of soda.

Exp. V. 20 grs. of cotton were treated in precisely the same manner, but as the difficulty of washing out the uncombined soda consumed much absolute alcohol, ordinary rectified spirits was employed instead. The soda compound weighed 21·28 grs., and yielded 2·05 grs. of sulphate of soda.

Exp. VI. 20 grs. of cotton similarly treated, were washed with hot alcohol of sp. gr. 825. The dried compound weighed 22·20 grs., and yielded 3·12 grs. of sulphate. This is a large amount, and indicates that alcohol of this strength may safely be employed to wash the compound.

Exp. VII. Lest it might be contended that the alcohol did not remove from the woody fibre certain impurities, which might be present in an aqueous solution of soda, 20 grs. of cotton were steeped in a clear but saturated alcoholic solution of the alkali. Little if any shrinking took place, but there was a certain amount of combination, for the cotton well washed with spirits of sp. gr. 825 and dried, weighed 21·01 grs., and afforded 1·41 grs. of sulphate of soda.

As yet the results are very discordant, as will be apparent from the annexed table, nor does the combined soda in any instance stand in a definite atomic ratio to the lignin :

	Ratio between original and soda-ed cotton			and combined soda.	
Exp. III.	100	:	109·85	:	5·91
,, IV.	100	:	105·45*	:	5·94
,, V.	100	:	106·4	:	4·49
,, VI.	100	:	111·0	:	6·83
,, VII.	100	:	105·05	:	3·08

* This number is reckoned as obtained from 20 grs.; but it is in all probability too low, since the whole amount of cotton, as will be afterwards explained, is never recovered from the mercerizing process.

From this we must conclude either that woody fibre has a great affinity for caustic soda at a low temperature, but does not form any definite chemical compound with it; or else that the cotton in the forementioned experiments had not been thoroughly saturated with the alkali. As this might depend upon the strength of the alkaline ley in which the immersion was made, a solution of soda of sp. gr. 1342 was employed, and gave much more satisfactory results.

Exp. VIII. 20 grs. of cotton steeped in soda-solution of the above-mentioned specific gravity, and washed with successive portions of hot alcohol of sp. gr. 825, until when dried it ceased to lose weight, was found to have increased to 22·64 grs., and yielded 4·25 grs. of sulphate of soda.

Exp. IX. 20 grs. of previously mercerized cotton, similarly treated, showed an increase of weight to 23·21 grs., and yielded 4·70 grs. of sulphate.

Exp. X. A piece of calico 4 in. × 4, and weighing, when thoroughly dried, 18·65 grs., was subjected to the action of soda. From a solution of sp. gr. 1124 it absorbed an amount of soda equivalent to 2·00 grs. of sulphate; that is, as 100 : 4·70 combined soda. Washed with water, dried, again immersed in alkaline ley, but of sp. gr. 1342, washed with hot alcohol of sp. gr. 825, and dried in vacuo, it weighed 21·84 grs., and yielded 4·40 grs. of sulphate of soda. The immersion in soda only lasted 10 minutes. The piece of calico had contracted to the measure of 3·3 in. × 3·3.

Exp. XI. In order to ascertain whether the fibre was capable of combining with a still larger proportion of soda, either by employing a stronger alkaline ley, or by exposing it to the action for a longer period, a piece of calico weighing 18·32 grs. was immersed for 17 hours in a solution of caustic soda so strong as to be syrupy, in a vessel protected from the atmosphere. Having been washed and dried as usual, it weighed 21·04 grs., and yielded 3·78 grs. of sulphate of soda. This, instead of being a larger amount of soda than in the three previous instances, is a trifle smaller. There was the same amount of contraction.

Exp. XII. was intended as one in which every precaution should be taken to insure the definite character of the compound examined. A piece of fine calico of about 90 strands to the inch, weighing 14·67 grs., and measuring 3 in. × 3, was steeped in cold caustic soda in a close vessel for 30 minutes. It was then removed, pressed between folds of cloth, and washed with absolute alcohol also in a vessel protected from the air, until it ceased to lose weight when dried. Dried

in vacuo it weighed 17·17 grs., and it afforded 3·15 grs. of sulphate of soda.

The results of these five experiments may be thus tabulated :

	Ratio between original and soda-ed cotton			and combined soda.	
Exp. VIII.	100	:	113·2	:	9·31
,, IX.	100	:	116·05	:	10·30
,, X.	100	:	111·2	:	10·34
,, XI.	100	:	114·8	:	9·07
,, XII.	100	:	117·05	:	9·41

It will be at once evident that there is a wide discrepancy between the numbers in the first column, but the second column presents considerable accordance; and, if we take the amount of soda in the experiment most to be relied on—No. XII., namely, 9·41 per cent, or the average of the whole five determinations,—namely, 9·68 per cent, we find it almost exactly coinciding with the amount that should be obtained, supposing one atom of soda to combine with one atom of lignine—$C_{24} H_{20} O_{20}$—namely, 9·65.

$$324 \quad : \quad 31·3 \quad :: \quad 100 \quad : \quad 9·65.$$

The mode of production of this substance might lead us to imagine that it was a substitution product of $C_{24} H_{20} O_{20}$, in which one equivalent of sodium replaced one equivalent of hydrogen; but, as the weight of the dried substance never fell short of the united weights of the cotton and the soda taken up, it must rather be considered as a compound of the two. The difference of its state of hydration clearly gives rise to the differences observable in the first column of the tables. In some instances (as Exp. X.) the soda appears to carry along with it little or no water, in other instances (as Exp. XII.) as large a quantity as 3 equivalents; and this combined water will not separate in vacuo at ordinary temperatures. The compound is also very hygroscopic, absorbing from moist air, in one observed instance, as much as 5·39 grs. of water for 23·21 grs. of "soda-ed" cotton, which however it parted with again in vacuo. When neutralizing with sulphuric acid the soda washed out from the cotton, I had frequently observed that there was no effervescence: this induced me to try whether the "soda-ed" cotton really did not absorb carbonic acid. Upon exposing a portion to an atmosphere of this gas, I found the alkali was converted into carbonate; and 20 grs. of cotton, which proved to be combined with 2·06 grs. of soda, weighed when dried in vacuo 23·71 grs. Little or no water could have been retained by the

substance, for the weight of the cotton, plus that of the alkali considered as carbonate, would be 23·51 grs.   There is a remarkable circumstance attending this compound in its relation to heat : it becomes scorched at a far lower temperature than the original cotton.

That the combination of the soda with the cotton has effected a permanent change upon it is certain ; when regained it is contracted, and takes dyes better ; but the question arises : Is this merely a physical alteration, or has a real chemical change of the lignina taken place ?   I am inclined to view the "mercerized" cotton as chemically identical with the original substance.   In the first place, it is of the same ultimate composition.   It is true, the cotton regained never absolutely equalled the original in weight ; but it was always observed that the fibre lost some flocculent portions during the steeping and the washing processes, enough to account for the 1 or 1·5 per cent deficiency which usually occurred.   The removal of only one equivalent of water would have occasioned a decrease of 2·78 per cent. Again, the mercerized cotton can be recombined with soda, causing even some additional shrinking by the process.   Mixed nitric and sulphuric acids convert it into gun-cotton ; it is acted upon by oil of vitriol just as ordinary lignine ; and it is similarly hygroscopic.

The change that takes place in the physical condition of the cotton is best observed under the microscope.   The fibres in their ordinary state appear as flattened twisted ribands ; but the moment they are touched by the alkaline ley they untwist themselves, and contract in length, as they swell out, assuming a rounded solid form ; and this circular appearance they retain after the soda is removed by water. Thus the shrinking is explained, and I think also the superior character of the colours which mercerized cotton is capable of exhibiting.   For the substance of the fibre itself is of a porous nature, and will of course absorb a larger quantity of the dye when expanded, than when compressed into a flat twisted band, and as this takes place in the same space, a greater *intensity* of colour must be the result.

From these observations it appears that lignine is capable of forming a combination with soda, the proportion of the alkial varying with the strength of the solution employed, but in no instance exceeding one atom, and that this compound is decomposed by water, being resolved into its original compounds.

In order to ascertain whether a similar potash compound existed, a piece of fine calico, measuring 3 in. × 3, and weighing 14·50 grs., was immersed for thirty minutes in as strong a solution of potash as

could be obtained limpid. It was washed with alcohol of sp. gr. 825, and dried and decomposed as usual. It shrank to the dimensions of 2·7 in. × 2·7. When combined with potash it weighed 17·14 grs., and it yielded 3·83 grs. of sulphate of potash.

	Ratio between original and combined cotton	and potash.
Exp. XIII. . . .	100 : 118·2	: 14·27

This shows that there was one equivalent of potash taken up by the cotton, the compound being $C_{24} H_{20} O_{20} + KO$.

$$324 : 47·3 :: 100 : 14·59.$$

These compounds of the alkalies with lignine are clearly analogous to their known compounds with sugar. Brendecke and others have shown that both cane- and grape-sugar will combine with potash and soda in the proportion of 1 equivalent, $C_{24} H_{20} O_{20}$, to 1 equivalent of the alkali. Whether these compounds are decomposed by water does not appear from the recorded observations; for whether it be so or not, the same phenomena would be presented. Disregarding the varying amount of water combined with the lignine compounds, we find both them and the sugar compounds expressed by the formulæ:

$$C_{24} H_{20} O_{20}. KO, \text{ and } C_{24} H_{20} O_{20}. NaO.$$
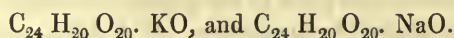
On a Compound Sulphate of Potash and Soda.

By J. H. Gladstone, Ph.D., F.R.S., F.C.S.

The saturating power of the common organic acids, is a subject to which great attention has been and still is paid. Many acids that were once considered monobasic have had their equivalents doubled or trebled, with evident advantage in the explanation of their salts. To take one example: Tartaric acid, formerly viewed as $HO, C_4H_2O_5$, is now represented as $2 HO, C_8H_4O_{10}$, and its bibasic character explains at once why, if half the quantity of potash necessary for its saturation be added to a solution of the acid, we obtain not a mixture of neutral salt and free acid, but a sparingly soluble bitartrate; and why we have such an endless variety of double tartrates, even one, Rochelle salt, in which the two alkalies, potash and soda, are united, although they are bases of the same natural family.

Chemists have more recently been led to inquire whether some of the inorganic acids usually esteemed monobasic, should not be also viewed as bibasic. It has been well remarked, that whilst some acids—as, for instance—nitric acid, always form neutral simple salts, others, of which sulphuric acid may be taken as a type, exhibit a great tendency to form acid and double salts. In fact, every reason which could be urged in favour of the bibasic character of tartaric acid would equally apply to sulphuric acid, excepting that we have no compound analogous to Rochelle salt. The argument is perhaps sufficiently strong even now; but could a double sulphate of potash and soda be prepared, the analogy would be complete; and none, I apprehend, who are accustomed to double the formula of tartaric acid, could refuse to view sulphuric acid also as $2 HO, S_2O_6$.

It was in the attempt to obtain such a salt that the compound now to be described was discovered.

Having occasion to prepare some salt which should show flashes of light on crystallizing, I followed the method recommended in Gmelin's "Handbook of Chemistry," Vol. I, p. 207. 2 parts of sulphate of potash, and 1 part of chloride of sodium, were fused together; the mass, removed from the crucible, was dissolved in boiling water, filtered, and suffered to cool. The result was very satisfactory. Small crystals separated, each at its formation emitting a luminous flash, visible even in shaded daylight. Their appearance struck me as being very uniform, yet certainly not that of sulphate of potash; and it occurred to me that they might be a double sulphate of the two alkalies. The crystals were examined by Mr. Crosby, of St. Thomas's Hospital, and were found to contain no water, but to give a precipitate with antimoniate of potash. They consisted of about 48 per cent of sulphuric acid, and 47 per cent of potash; the remaining 5 per cent, or thereabouts, being soda. This was quite inconsistent with the formula KO, NaO, S_2O_6; but it might well contain such a compound, mixed with ordinary sulphate of potash.

A series of experiments was set on foot in order to obtain, if possible, pure crystals of this supposed salt. The salts obtained were freed from hygroscopic moisture by heating them; sulphuric acid was determined in the usual way as baryta-salt, and the potash as platinum-salt. Every analysis that was made by me is recorded.

Exp. 1. A crop of large crystals was obtained by the process already described. They were very regular in form—six-sided prisms, terminating in six-sided pyramids, truncated.

Salt employed.	Sulph. baryta obtained.
38·18 grs.	53·10 grs.
27·61 ,,	38·65 ,,

Salt employed.	Chlor. plat. and pot. obtained.
13·83 grs.	33·32 grs.

The acid and base thus determined are in the proportion :

Sulphuric acid   47·77 and 48·06 per cent
Potash .   .   .   46·58   ,,

Now, in order to obtain such numbers as these, we must suppose that 6 equivs. of sulphuric acid are combined with 5 of potash and 1 of soda.

	Equivs.	Calculated.	Average of experiments.
Sulphuric acid	6	47·26	47·91
Potash . . .	5	46·57	46·58
Soda . . .	1	6·16	5·34
		100·00	100·00

Exp. 2. One part of sulphate of potash was mixed with two parts of crystallized sulphate of soda, that is, about equivalent proportions; water was expelled from the mixture by heat, and the salts were fused together. The cooled mass was dissolved in hot water, which presently afforded crystals similar in appearance to the preceding. They were dried and analyzed.

Salt employed.	Salt obtained.
32·64 grs.	45·60 grs. sulph. of baryta.
14·65 ,,	35·81 ,, chlor. plat. pot.

These numbers indicate:

Sulphuric acid   47·96 per cent
Potash . . .   47·26   ,,

This salt is evidently identical with the preceding.

Exp. 3. One part of sulphate of potash and two parts of crystallized sulphate of soda were dissolved together in water by the aid of heat. There separated on cooling, small crystals, of a perfectly definite appearance, six-sided prisms with six-sided pyramids at the ends, truncated. They were analyzed as before.

Salt employed.	Salt obtained.
10·20 grs.	14·41 grs. sulph. baryta.
8·31 ,,	19·31 ,, chlor. plat. pot.

These numbers indicate:

Sulphuric acid   48·49 per cent
Potash . . .   44·92   ,,

These results differ but little from those previously obtained.

Exp. 4. A mixture of *equal* parts of sulphate of potash and chloride of sodium fused together and dissolved in hot water, afforded crystals which were evidently the same.

Exp. 5. Three parts of bisulphate of potash and one part of chloride of sodium were fused together. Hydrochloric acid was given off in large quantity, as might be expected; and on dissolving the fused mass in hot water, and suffering it to cool, there separated

hexagonal crystals, apparently identical with those previously examined, mixed with another salt in feathery flakes.

Exp. 6. The same salts, mixed in the same proportions, were boiled together for a considerable time in water. The solution yielded the feathery flakes above mentioned, along with crystals that appeared to be thin segments of hexagonal prisms, but which Dr. Leeson, by a minute examination of their angles, found to be derived from the octagon of the regular system by the development of two of the opposite planes. They were found to contain soda, and no water. On analysis, they yielded the following results:

Salt employed.	Salt obtained.
25·09 grs.	35·12 grs. sulph. baryta.
14·17 ,,	33·20 ,, chlor. plat. pot.

which indicate:

Sulphuric acid	48·05 per cent
Potash . . .	45·29 ,,

As the microscope showed some small needle-shaped crystals sticking to these octagonal ones, a portion of the salt was washed several times with a very little cold water, and analyzed.

Salt employed.	Salt obtained.
7·51 grs.	10·37 grs. sulph. baryta
6·00 ,,	14·22 ,, chlor. plat. pot.

which indicate:

Sulphuric acid	47·40
Potash . . .	45·83

Another portion of salt was prepared from the same source, recrystallized, and then washed with a little cold water. The crystals were small, but of the same form as the first. They were analyzed.

Salt employed.	Salt obtained.
21·46 grs.	29·61 grs. sulph. baryta
7·23 ,,	17·49 ,, chlor. plat. pot.

which indicate:

Sulphuric acid	47·37 per cent
Potash . . .	46·75 ,,

All these results seem to point out a salt similar in composition to all those previously examined.

Exp. 7. A saturated solution of carbonate of soda was added to a saturated solution of bisulphate of potash until effervescence ceased.

A crystal or two separated. The solution yielded on evaporation a crop of crystals, bearing a general resemblance to the salt formerly obtained. They were dried and analyzed.

Salt employed.	Salt obtained.
24·42 grs.	33·95 grs. sulph. baryta
12·06 ,,	27·40 ,, chlor. plat. pot.

which indicate :

Sulphuric acid   47·73 per cent
Potash . . .   43·92   ,,

differing little from previous estimations.

Exp. 8. One part of nitrate of potash and two parts of crystallized sulphate of soda, dissolved together, and evaporated, gave crystals of the compound salt, mixed with nitre.

Exp. 9. In order to see whether the same salt would form in the presence of a large excess of acid, 3 ounces of sulphate of potash, 6 ounces of crystallized sulphate of soda, and nearly 2 fluid ounces of sulphuric acid, were boiled together in water, and evaporated. The crystals, which were small, and of the ordinary shape, were slightly washed with cold water, dried, and analyzed.

Salt employed.	Salt obtained.
27·78 grs.	39·17 grs. sulph. baryta,

which indicates :

Sulphuric acid   .   .   48·40 per cent.

This scarcely exceeds the previous determinations of sulphuric acid. The salt was evidently the same.

Exp. 10. Conversely, the effect of an alkaline solution was tried. Two parts of sulphate of potash and one part of hydrate of soda were dissolved together in water. The evaporated solution gave a crop of very minute crystals. They were washed with a little cold water two or three times, dried over sulphuric acid, and analyzed.

Salt employed.	Salt obtained.
18·39 grs.	25·61 grs. sulph. baryta,

which indicates :

Sulphuric acid .   .   47·81 per cent.

Hence the salt was identical with those analyzed before.

Exp. 11. Thinking that a large excess of soda might cause the formation of a salt richer in soda, 6 parts of that sulphate, crystallized, were dissolved in water with 1 part of sulphate of potash, and evaporated. Crystals of common sulphate of soda alone separated.

On another occasion, when 1 lb. of sulphate of soda had been dissolved along with ½ lb. of sulphate of potash, the solution yielded, first, six-sided prisms, with dihedral summits, containing soda; then large crystals of sulphate of soda; and the mother-liquor from them yielded again a crop of the compound salt.

It appears, then, that all these attempts have failed to produce a sulphate of potash and soda analogous to the double tartrate; but they invariably yielded a compound salt containing a small amount of soda. This has all the appearance of being definite and uniform, and seems to consist of sulphuric acid, combined with 6 equivs. of base, 1 being soda and 5 potash. Its formula decides nothing in favour of the bibasic character of sulphuric acid, but it does not militate against such a view: it may be written $5 KO, NaO, 3 S_2O_6$, though perhaps chemists will generally prefer the expression $5(KO, SO_3) + NaO, SO_3$.

It may be asked, why was not the salt subjected to repeated crystallizations before it was analyzed? The reason was, that I feared some alteration in the salt during such a process; indeed, a specimen which had thus been treated, was found to have lost 1 per cent of sulphuric acid, showing a considerable decrease in the amount of soda.

Salt employed.	Salt obtained.
26·11 grs.	35·38 grs. sulph. baryta.
25·05 ,,	34·08 ,,

which indicate :

Sulphuric acid, 46·52 and 46·70 per cent.

Had the salt been entirely reduced to ordinary sulphate of potash, analysis should have given only 45·94 per cent.

The solubility of this compound salt was found to be very similar to that of sulphate of potash itself: 1000 parts of water at 212° F. were found capable of dissolving 250 parts; at 55° F., 101 parts; and at 40° F., 92 parts of the salt. 25 grs. of salt, recrystallized during this experiment, was found to yield 34·11 grs. of sulphate of baryta, indicating 46·90 per cent of sulphuric acid.

The crystalline form, also, is the same as that of sulphate of potash; but the crystals appeared to me more uniform than that salt ordinarily is, and having not so great a tendency to become long and branching. The compound and the simple salt are both alike anhydrous.

Since performing these experiments, I have consulted the original paper of Rose, in Pogg. LII, " *Ueber die Lichterscheinungen bei*

der Krystallbildung."   I find he has accurately described the crystals which emit light, but his quantitative determinations led him to doubt their definite character; I, however, have always found them uniform in composition, in whatever manner they may have been produced.   Their production, indeed, under such various circumstances, could not have been anticipated; and they form a remarkable instance of a certain proportion of the base of a salt being replaced by an analogous oxide, without materially affecting its physical properties.

ON

THE RELATIONS

BETWEEN THE

ATOMIC WEIGHTS OF ANALOGOUS

ELEMENTS.

BY

J. H. GLADSTONE, PH.D.

CHEMISTS who have turned their attention to the series of numbers representing the atomic weights of the elementary bodies, have frequently remarked curious relations between them. It is between similar elements that these numerical relations occur; and to such an extent is this the case, that Berzelius, after mentioning numerous instances, says, "We see that bodies which present the same properties up to a certain point have certain relations between their atomic weights*."

To illustrate this statement, to show the extent of its truth, and to draw certain analogical inferences tending to the proper understanding of such a fact, are the objects of this communication.

The following is a list of the atomic weights arranged from the lowest to the highest, and thus without any reference to chemical relationship. The numbers adopted are those given in the last volume of Liebig's *Jahresbericht*.

1	Hydrogen.	14	Nitrogen.
4·7	Glucinum.	16	Sulphur.
6	Carbon.	19	Fluorine.
6·5	Lithium.	20	Calcium.
8	Oxygen.	21·3	Silicon.
10·9	Boron.	22·4	Zirconium.
12	Magnesium.	23	Sodium.
13·7	Aluminium.	25	Titanium.

* *Traité de Chimie*, vol. iv.

26·7	Chromium.	58	Tin.
27·6	Manganese.	59·6	Thorinum.
28	Iron.	60	Uranium.
29·5	Cobalt.	64·2	Tellurium.
29·6	Nickel.	68·5	Barium.
31	Phosphorus.	68·6	Vanadium.
31·7	Copper.	75	Arsenic.
32·6	Zinc.	80	Bromine.
35·5	Chlorine.	92	Tungsten.
39·2	Potassium.	98·7	Platinum.
39·5	Selenium.	99	Iridium.
43·8	Strontium.	99·6	Osmium.
46	Molybdenum.	100	Mercury.
47	Cerium.	103·7	Lead.
47	Lanthanium.	108·1	Silver.
50	Didymium.	127·1	Iodine.
52·2	Rhodium.	129	Antimony.
52·2	Ruthenium.	184	Tantalum.
53·3	Palladium.	197	Gold.
56	Cadmium.	208	Bismuth.

If we glance at this list we notice some peculiarities, but no very striking ones. We might ask, for instance, Why should there be so many elements congregated about No. 28; and, again, about 52? Why should there be only one atomic weight between 80 and 92, and then a group of four?

The following letter, kindly sent me by Professor De Morgan, will give the data for calculating the probabilities of this. I introduce it on account of its applicability, not only to this particular case, but to others which will occur in these observations.

"Univ. Coll., Lond., Dec. 18, 1852.

"DEAR SIR,—The following, though but an imperfect view of the whole question, will be enough, I think, for your purpose. I send formula and all, that who likes may verify it.

"If there be n numbers, each of which may be drawn at any trial, and all equally likely, and if the following denominations be used,

$$P = \left(1 - \frac{1}{n}\right)^m$$

$$Q = m \cdot \left(1 - \frac{1}{n}\right)^{m-1} \cdot \frac{1}{n}$$

$$R = m \frac{m-1}{2} \left(1 - \frac{1}{n}\right)^{m-2} \frac{1}{n^2}$$

$$S = m \frac{m-1}{2} \frac{m-2}{3} \left(1 - \frac{1}{n}\right)^{m-3} \frac{1}{n^3}, \&c.$$

Then, speaking of one assigned number, the chance that that number shall not appear in m trials, is P; that it shall appear once and once only, is Q; twice and twice only, is R; and so on. Further, the chance that it shall appear once or more is $1 - P$. That it shall appear twice or more, the chance is $1 - (P + Q)$. Three times or more, $1 - (P + Q + R)$; and so on.

"For calculation,

$$Q = \frac{mP}{n-1}$$

$$R = \frac{(m-1)Q}{2(n-1)}$$

$$S = \frac{(m-2)R}{3(n-1)};$$

and so on.

"Let there be 100 numbers, and 60 trials to be made. I find

$$P = \cdot 54716$$
$$Q = \cdot 33161$$
$$R = \cdot 09881$$
$$S = \cdot 01929$$
$$T = \cdot 00278$$
$$U = \cdot 00031$$
$$P + Q + R + S + T + U = \cdot 99996$$
$$1 \cdot 00000$$

$\cdot 00004$.   Chance of six or more of a given number.

"It is then 99996 to 4, or 24999 to 1, against the appearance of a predicted number six or more times.

"Now suppose the question to be what is the chance that *some one* number, not named, shall occur six or more times; that is, either the one named in the last case, or some other? This is a much more complicated question, but it is certain that 100 times the chance in the last is too great. Now $\cdot 00004 \times 100 = \cdot 004$, which is too much decidedly. Consequently 996 to 4, or 249 to 1, are too small odds to lay against the appearance of some one number six or more trials.

"That is, you may lay more than 250 to 1 that of all the numbers, *no one* will occur six or more times in 60 trials.

"I am, dear Sir,

"Yours faithfully,

"*Dr. Gladstone.*"   "A. DE MORGAN."

Reverting to the list of elements given above, we certainly

find no recurrence of certain numbers, or other peculiarity, sufficiently striking to warrant us in drawing any inference; but let us arrange the elements according to their chemical relations, and the case will be entirely altered. Any arrangement of the elements is attended with difficulty: I shall not attempt to form one of my own, as it would be open to the objection that my mind had been biassed by dwelling upon the numerical relations; but I shall adopt that given in Gmelin's Handbook of Chemistry at the commencement of vol. ii.

O		N			H
F Cl Br I					L Na K
S Se Te					Mg Ca Sr Ba
P As Sb				G Er Y Tr Ce Di La	
C B Si				Zr Th Al	
Ti Ta Nb Pe W				Sn Cd Zn	
Mo V Cr		U		Mn Co Ni Fe	
Bi	Pb	Ag	Hg Cu		
Os Ru	Ir	R	Pt Pd	Au	

Even here many elements are grouped together which have but a faint chemical resemblance. Thus tin has little in common with cadmium and zinc, or mercury with copper; fluorine is very different from the other halogens; magnesium can scarcely rank with the metals of the alkaline earths; whilst late researches have shown the strict isomorphism of chromium with manganese or iron.

If we substitute the equivalent numbers in this arrangement, the slightest glance will make us acquainted with many remarkable resemblances. Decimals are omitted for the sake of brevity.

8		14			1
19, 35, 80, 127					6, 23, 39
16, 39, 64					12, 20, 44, 68
31, 75, 129				5, —, —, —, 47, 50, 47	
6, 11, 21				22, 60, 14	
25, 184, —, —, 92				58, 56, 33	
46, 69, 27		60,		28, 29, 30, 28	
208, 104,	108,		100, 32		
100, 52, 99,	52,		99, 53, 197.		

Looking more closely into this arrangement of numbers, we shall find the observation of Berzelius borne out in every instance, but one, of a well-defined chemical group.

These numerical relations are of three kinds. The atomic weights of analogous elements may be the same; or may be in multiple proportion; or may differ by certain increments.

Of the first class we remark the strictly analogous metals,—chromium 26·7, manganese 27·6, iron 28, cobalt 29·5, and nickel 29·6. Then a double group of the platinum ore metals:—palladium 53·3, rhodium, 52·2, and ruthenium 52·2; and also platinum 98·7, iridium 99, and osmium 99·6. We are tempted to add to this—mercury 100. Again, in the mineral cerite we find together—cerium 47, lanthanium 47, and didymium 50. It has been remarked, not only that the metals of each of these groups have similar properties and weights, but that they are found associated together in nature. The question has often been put,—Would more accurate determinations show these atomic weights to be not nearly but exactly the same? It may be doubted. Yet it ought to be remembered that these numbers are the actual results of experiment, and are not controled by any theory, as is always the case with organic compounds.

As to the second class of numerical relations among atomic weights, namely, multiple proportions, Who has failed to remark that the platinum group has double the atomic weight of the palladium group, and that gold 197 is again the double of platinum? These two pairs have frequently been noticed—boron 10·9, and silicon 21·3; oxygen 8, and sulphur 16. We now come to a large group, those metals whose oxides principally affect an acid character, being also insoluble in water. The highest of these in weight is tantalum 184; half 184 is 92—the equivalent of tungsten; half 92 is 46—the equivalent of molybdenum; and half 46 is 23—just below the recognized equivalent of titanium 25*. Three times 23 is 69: now 68·6 is the equivalent of vanadium, being intermediate between tungsten and molybdenum. Tin has certain claims to be grouped along with the same elements; its equivalent is 58: now 57·5 would be two and a half times 23, and intermediate between molybdenum and vanadium. Taking 11·5 as the basis number of this series, we have—

			Received equiv.
Titanium	. .	$2 \times 11\cdot5 = 23$	25
Molybdenum	.	$4 \times 11\cdot5 = 46$	46
Tin	. . . .	$5 \times 11\cdot5 = 57\cdot5$	58
Vanadium	. .	$6 \times 11\cdot5 = 69$	68·6
Tungsten	. .	$8 \times 11\cdot5 = 92$	92
Tantalum	. .	$16 \times 11\cdot5 = 184$	184

* 23·6 according to Mosander.

Silicon is certainly very similar to the first of this group, titanium, but its atomic number 14·2 (reckoning silica to be SiO^2) is unconformable.

These metals, whose numbers have a multiple relationship, are not remarkable for being found together in nature.

The third kind of relationship is where an element, having properties intermediate between those of two other elements, has the intermediate atomic weight. Four instances of this have been noticed*. We observe all four groups in the arrangement of Gmelin given above. They are—

The metals of the alkalies :—

　　　　Lithium, 6·5.　Sodium, 23.　Potassium, 39·2.

The metals of the alkaline earths :—

　　　　Calcium, 20.　Strontium, 43·8.　Barium, 68·5.

The halogens :—

　　　　Chlorine, 35·5.　Bromine, 80.　Iodine, 127·1.

Sulphur and its congeners :—

　　　　Sulphur, 16.　Selenium, 39·5.　Tellurium, 64·2.

The members of the last two groups generally occur together in nature.

There are certain analogies which may perhaps lead us to some understanding of these facts.

First, in the case where there is the same atomic weight. If the allotropism of an element were carried through all its compounds, we should have what occurs in the iron and similar series. The only partial instances of this which I remember are the sulphides of phosphorus, as remarked by Berzelius, and silicic acid, the two conditions of which bear a striking analogy to the two allotropic forms of the elementary silicon itself.

Secondly, in the case of multiple atomic weights, is there not something analogous to the polymerizing of which we have many examples in organic chemistry ? or to the modifications of a metal, such as mercury, where we have 100 or 200 parts combining with 1 equivalent of chlorine to form a salt ? the difference in this latter case being, that when we regenerate the metal, from whatever source, it is always the same mercury.

Thirdly, in the case where an element of intermediate properties has an intermediate atomic weight. I regard this as strictly analogous to the series of homologous bodies so common in organic chemistry. My meaning may be best explained perhaps by a reference to the quasi-metals, or compound hydrogens. We have hydrogen 1, methyle 15, æthyle 29, amyle 71 : the com-

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* See Gmelin's Handbook of Chemistry, part 1. Dumas also brought forward some speculations on these groups at the Ipswich Meeting of the British Association.

pounds of these bodies differ progressively in properties—the boiling-point for instance—and they occur together in the processes of their preparation. Methyle is intermediate in chemical characters between hydrogen and æthyle, and has the intermediate atomic weight $\frac{1+29}{2}=15$. If we did not know in what respect the one quasi-metal differed from another, we should have a series of bodies precisely analogous to the metals of the alkalies: but we do know it; we know that methyle is hydrogen plus a certain increment $C^2 H^2$; æthyle is hydrogen plus twice $C^2 H^2$, &c. The general expression for any such homologous series is, taking x as the increment,—

$$a; \quad a+x; \quad a+2x; \quad a+3x, \&c.$$

This will equally apply to any other cases of the addition of increments—the conjugate organic acids, such as formo-benzoic acid, or the series phosphoric acid PO^5, 71, azophosphoric acid $P^2 NO^5$, 116, and deutazophosphoric acid $P^3 N^2 O^5$, 161. Now it is precisely in like manner that I regard these series of elements: I view sodium as lithium plus a certain increment; in fact, $Na = L + x$, and $K = L + 2x$. Lithium is here the starting-point, the "hydrogen" of the series; and so in like manner are calcium, chlorine, and sulphur. We do not know what the increments are, but we know their atomic weights.

In the lithium series it is 16·3
  ... calcium   ... 24·2
  ... chlorine   ... 45·8
  ... sulphur   ... 24·1

It is remarkable that the increments of the calcium and sulphur series are the same in weight—24, and that the increment of the lithium series should be almost exactly two-thirds of that number.

Why should this numerical relation always give us triads? As yet we have no instance of a fourth member of one of these series, unless indeed we view the titanium series in this light; but the advance of science may furnish us with such instances if my theory of increments be correct. Whether any element not contained in these groups have the atomic weight of some other plus a certain increment, cannot be known until we have a third member of the series to prove the fact. Thus we can only speculate upon the curious circumstance, that zinc and cadmium—two similar metals occurring together in nature—have atomic weights differing almost by the remarkable number 24. Zn $32·6 + 23·4 = 56$ at. wt. of Cd.

`I believe that, with one exception, every well-defined group of elements has been considered under these three classes. That exception is in the case of arsenic and antimony, which are unquestionably analogous, phosphorus being also closely allied to them : the three are placed together in Gmelin's arrangement, but I see no ratio between their numbers 31, 75, 129. Schrœtter's reduction of the equivalent of phosphorus has prevented our considering antimony, 129, as four times that element. It is, however, double tellurium, 64·2, which is in some respects an analogous body.

There are several elements, such as bismuth, which have no very evident analogues ; and of others which are similar we cannot speak, because we are ignorant of their atomic weights. These are pelopium and niobium, and yttrium erbium and terbium.

Alumina is usually classed with the earths ; but its compounds are strictly isomorphous with those of the sesquioxides of the iron group. The equivalent of aluminium, 13·7, happens to be half of theirs. Again, glucina is certainly an analogous earth ; viewing it also as a sesquioxide, the equivalent of glucinum is 7, which is half that of aluminium.

Some of the properties of lead would ally it to the family of the alkaline earths, but there is no apparent numerical relation : in other points it resembles silver, with which it is so generally found ; their respective equivalents are 103·7 and 108·1, but neither the resemblance of chemical properties nor of number is very close. I would rather not consider it an instance of the general law.

Whatever may be thought of some of the speculations towards the close of this paper, these numerical relations are indisputable facts. That we should frequently find relations between 56 numbers drawn at hazard from a range little exceeding 100 might be predicted from the laws of probability, but that this should be to a considerable extent coincident with chemical relationship is not probable. Still more is it against all probability that, by mere chance, whenever, with one exception, close analogy of properties exists, there exists also numerical relationship ; and although we cannot now see the precise reason of this, we can scarcely imagine that the intimate constitution of these related elementary bodies will long remain an unfruitful field of investigation.

On the Corrosive Action of Sugar on Iron and other Metals.

By J. H. GLADSTONE, Ph.D., F.R.S.

Owners of iron-built ships frequently object to sugar freights, alleging that the saccharine juices which exude from the casks rust the metal deeply. In sugar refineries also it has occasionally happened that portions of machinery made of iron have been wholly dissolved. Starting from these assertions of practical men, I have made the following observations.

If a piece of iron be partially immersed in a solution of pure cane-sugar, and it be set aside in a rather warm place, where air has access to it, the metal will soon become deeply corroded about the edge of the liquid; but that portion which is permanently immersed will remain bright for a considerable space of time. The solution then contains protoxide of iron, which, absorbing oxygen from the atmosphere, presently separates as the sesquioxide, and subsides in the form of a red powder, leaving the sugar free to exert its influence again upon the metal. In this manner, the action becomes continuous, the organic principle acting as a carrier of oxygen; and we can readily understand how a small quantity of sugar may eat into a large sheet of iron.

A definite compound seems to be formed by the oxide of iron and sugar. It is very soluble in water, but insoluble in alcohol. Its solution is of a deep red-brown colour. It has the peculiar astringent flavour usually belonging to iron salts. The addition of ammonia or potash does not cause the precipitation of the metallic oxide; neither do alkaline carbonates; but a black precipitate is obtained at once on the addition of sulphide of ammonium, and a pale blue colour is produced by the ferrocyanide of potassium, and a deeper blue by the ferridcyanide. Nitric acid causes at once the formation of nitrous fumes, after which, neutralisation by an alkali produces an abundant precipitate of the sesquioxide. When boiled with sulphate of copper, the red oxide also precipitates. A stream of hydrosulphuric acid passed through the solution, throws down the whole of the iron as sulphide, and leaves a perfectly neutral solution, containing nothing that could be distinguished from the uncombined sugar.

This compound, then, evidently consists of protoxide of iron, with sugar but little, if at all, altered. The determination of the proportions in which these substances are combined is attended with difficulty, for the substance itself shows not the slightest disposition to crystallise; and the separation of it from uncombined sugar by means of alcohol was not found to be sufficiently practicable. The most likely way to obtain a pure substance appeared to be by allowing the sugar to saturate itself gradually with the metallic oxide.

Accordingly, some sugar solution, which had been left in a warm place with iron for eighteen months, and had evaporated to dryness during that time, was examined. When redissolved in water it contained no sugar, unless in combination with the metallic oxide; but it was not identical with the preceding compound. It was insipid, with a slight ferruginous after-taste. The action of different reagents upon it was much the same as upon that first produced; but it was much more stable, not being affected by the oxygen of the atmosphere. A stream of hydrosulphuric acid caused only a partial decomposition, setting free a substance which had a decidedly acid reaction to test-paper, though an insipid taste. The acid thus partially separated was capable of dissolving fresh oxide of iron, but did not attack the metal itself, though immersed in it for some days.

A portion of the compound just described was evaporated to dryness in a water-bath, weighed, incinerated in a platinum crucible with the addition of a few drops of nitric acid to ensure the complete oxidation of the metal, and the sesquioxide of iron weighed.

$$\text{Sugar compound taken} \quad . \quad . \quad 6\cdot603 \text{ grm.}$$
$$\text{Sesquioxide of iron obtained} \quad . \quad 1\cdot263 \quad ,,$$

which is equivalent to $1\cdot136$ grm. of protoxide of iron, or $17\cdot20$ per cent.

This is almost precisely what ought to be obtained from a compound of single equivalents of oxide of iron and sugar:—

	Calculated.	Found.
Protoxide of iron . . .	17·39	17·20
Sugar	82·61	82·80
	100·00	100·00

However, this must be taken rather as an approximative than as an exact expression of its composition. It is, indeed, not unlikely that the assumption of acid properties was accompanied by a slight oxidation of the organic principle. From the analogy of the baryta and lime compounds of sugar, in which that substance loses one equivalent of the elements of water in combining with the oxide, we should expect the formula of the compound first formed to be $C_{12} H_{10} O_{10}$, Fe O.

It is probable that these two are not the only compounds produced by the action of sugar on iron; for, although no indications were observed of any soluble compound of the sesquioxide, yet the red powder deposited from the solution contained more or less of some organic principle in intimate combination.

Since sugar attacks a mass of iron so readily, it seemed highly probable that it would dissolve the oxide easily; but such was not

found to be the case.   Some freshly-precipitated protoxide of iron, which had been well washed, was boiled in a solution of pure sugar, and set aside with it for a period of twenty-four hours in an air-tight vessel, but not a trace of iron was found in the solution.   A second experiment was made, in which the oxide of iron was presented in a nascent condition to the organic principle; a solution of pure cane-sugar being mixed with one of sulphate of iron, and the whole being just supersaturated with potash.   The precipitated protoxide was separated by filtration; the solution, which was at first perfectly clear, soon became turbid from the formation of sesquioxide, but the amount of iron actually dissolved was extremely small.   That the solution of even this trace depended upon the presence of the alkali, appears probable from a third experiment, where a large excess of potash was added to a similar mixture of sugar and sulphate of iron, and a deep red solution was obtained containing a large quantity of the metallic oxide.   This solution, when freely exposed to the air, showed very little sign of absorbing oxygen.   As a supplement to this experiment, some freshly precipitated and washed protoxide of iron was mixed with a quantity of potash in a solution of sugar contained in an air-tight vessel.   After the mixture had stood awhile, protoxide of iron was found in solution; but it existed in but very small quantity, even after the expiration of a month.

In order more fully to determine the nature of this action of sugar on iron, a piece of that metal was immersed in a solution of pure sugar in a glass tube inverted over mercury, in such a way as to exclude the access of air and to retain any gas that might be formed. After the lapse of three months, it was found that not a particle of any permanent gas had been formed, and the solution remained very nearly as colourless as at first.*   It thus appears that the sugar does not attack the iron as an acid does—by causing the replacement of hydrogen by the metal, and the consequent evolution of that element in the gaseous form.   The presence, too, of free oxygen appears necessary to the action; and yet it has been seen by previous experiments that it is difficult to get sugar to combine with the oxide itself unless an alkali be present, when doubtless a different compound is formed.

Experiments were tried with various strengths of the saccharine solution, and with brown as well as white sugar; and in every case the iron was attacked.   In order to test the effect of salts in conjunction with the sugar, pieces of iron were placed in five vessels containing equally strong solutions of cane-sugar, to four of which

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* In a similar manner, iron vessels are employed without risk in sugar refineries, where the vessel is always kept filled with the saccharine solution.

had been added respectively chloride of sodium, chloride of ammonium, nitrate of potash, and sulphate of magnesia. After awhile, protoxide of iron was found in all the five solutions, and there was about an equal deposit of the sesquioxide in the different cases. The addition of chloride of sodium to a mixture of freshly precipitated protoxide of iron and sugar, did not cause combination to take place between them. A piece of zinc placed in contact with iron in the sugar solution, was found not to prevent the dissolving of that metal, but both were attacked.

The effect of a solution of sugar upon other metals was tried; but none was found to be affected by it to an extent at all comparable with iron.

Copper.—Considering the great influence which the presence of sugar exerts in preventing the precipitation of oxide of copper, it might be anticipated that it would exhibit an action on the metal itself analogous to that already described. But it is not so. In an experiment made in the summer time, a few weeks' exposure of pieces of copper to a sugar solution showed a trace of the metal dissolved; but in the winter time, an exposure of seven months' duration merely produced a very faint blueness of the saccharine liquid, which was scarcely blackened by the addition of sulphide of ammonium.

Lead.—Lead was attacked much more readily. Three days' exposure in warm weather, a few weeks in cold weather, or a few hours at a boiling temperature, produced a solution which was distinctly blackened by a soluble sulphide.

Zinc.—This metal was very slowly acted upon. Seventeen days' exposure in warm weather was found to give a solution containing some oxide of zinc; but about forty hours' boiling did not cause the solution of a sufficient quantity to be detected by the ordinary reagents. In the experiment where iron and zinc in contact were exposed to the sugar, a much larger proportion of the zinc appeared to be dissolved; after the oxidation of the iron by nitric acid and the removal of the oxide by ammonia, the alkaline solution gave a copious white precipitate when tested with hydrosulphuric acid.

Tin.—Tin was also very slowly attacked. The small quantity at any time found dissolved was in the condition of the binoxide. In an experiment in which the sugar solution was boiled with pieces of this metal for perhaps forty hours, no indication of it in the liquid was obtained.

Mercury and *Silver.*—These metals were not found to be acted upon by sugar in the slightest degree.

Royal Institution of Great Britain.

1854.

WEEKLY EVENING MEETING,

Friday, March 31.

Col. Philip J. Yorke, F.R.S. President of the Chemical Society,
in the Chair.

John Hall Gladstone, Esq., Ph. D., F.R.S.

On Chemical Affinity among Substances in Solution.

An historical sketch of the development of the ideas of chemists
concerning "Affinity" was first given. The dogma of Hippocrates
that "Like combines only with like," was shewn to be superseded
by the view of Glauber and others, that unlike substances com-
bine most readily: and that where two bodies have an affinity *for*
one another, it is a sign that they have *no* affinity *with* one another.
The views of Newton and Boyle in reference to the different de-
grees of strength of affinity were then considered, and particular
attention was directed to the doctrine of Bergmann, that when a
decomposition takes place by means of the greater elective attrac-
tion of a third body, that decomposition is complete. In op-
position to this, Berthollet contended that in all such cases of
composition, or decomposition, there takes place a partition of the
base, or subject of the combination, between the two bodies whose
actions are opposed; and that the proportions of this partition are
determined, not solely by the difference of energy in the affinities,
but also by the difference of the quantities of the bodies,— by their
physical condition,— and by that of the combinations capable of
being generated. These views did not meet with a favourable
reception at the time of their promulgation; and the attention of
chemists had been drawn away from the subject until within these
last few years, when Malaguti, Bunsen, Debus, and Williamson, have
published investigations bearing upon the point. The Lecturer then
stated that before any of these papers had appeared, he had been
thinking of and performing some experiments upon the subject in
question, and that he was still continuing them.

After a few experiments illustrative of "Chemical combination"
and of "Elective Affinity," others were introduced to show how
easily this latter phenomenon was affected by circumstances. Thus
ammonia will displace alumina from a solution of the sulphate, but

on the other hand, alumina will displace ammonia when heated with the solid sulphate of that volatile base; whilst if solutions of chloride of aluminum and sulphate of ammonia be mixed and evaporated, crystals of the double sulphate, ammonia-alum, will appear.   There were on the table two white salts; the one had been carbonate of baryta, but by boiling with excess of sulphate of potash, it had been converted into the sulphate; the other had been sulphate of baryta, but by long continued boiling with much carbonate of potash, it had suffered the opposite change into the carbonate.   The Lecturer then stated that so great is the influence exerted by these various circumstances, that some have doubted whether there be a true " elective affinity;" he however believed that after making every allowance for known causes there is still a residuary phenomenon to which that name is the most appropriate.   Allowing then, with Bergmann, that relative degrees of affinity exist, the question arises:— Is Berthollet's law also correct?   It is very difficult to arrive at a satisfactory answer, since it is almost impossible to eliminate other influences.   Several reactions, however, were mentioned as tending to show that there is some truth in the law:— for instance, the solution of gold in hydrochloric acid upon the addition of nitrate of potash.   The experiments of Bunsen on mixtures of carbonic oxide and hydrogen, exploded with a quantity of oxygen insufficient for complete combustion; and those of Debus on the precipitation of mixed hydrates of lime and baryta by carbonic acid, were explained; as also the remarkable fact noticed by both, that the resulting products were always in certain atomic proportions to one another.   But in both these cases the first products of the chemical action are removed at once from the field: it is quite another case when they remain free to act and react on one another. Supposing they all remain in solution, the requisite is fulfilled; but how are we to know what has then taken place?   Malaguti thought to obtain an indication of this by mixing the aqueous solutions of two salts, one of which is soluble in alcohol, and the other is insoluble, and then pouring them into very strong alcohol, and analyzing the salts immediately thrown down.   His results are tabulated; they are valuable, but to some extent open to objection on account of the disturbing influence of the alcohol.   Some observations of Professor Graham, and others of Professor Williamson, as yet unpublished, were then spoken of, and the Lecturer proceeded to describe his own endeavours to arrive at a knowledge of the intimate constitution of a mixture of salts in solution by observing their physical properties, especially colour.

If solutions of one equivalent of nitrate of iron, and a triple equivalent of sulphocyanide of potassium be mixed, a blood-red colour results owing to the formation of sulphocyanide of the sesquioxide of iron; the question arises—Has all the iron left the nitric acid to unite itself with the sulphocyanogen?   It has not; for on the addition of equivalent after equivalent of sulphocyanide of potassium,

a deeper red is constantly obtained. The arrangement by which this deepening of colour was quantitatively determined was explained, and imitated on the lecture table. The result was that even up to 375 equivalents, a regular increase was observed to take place, more rapidly at first than afterwards, which was exhibited to the eye by the results being projected as a curve. Again, as in the mixture of equal equivalents of the two salts, some iron still remains in combination with the nitric acid, a portion of the potassium must still remain united to the sulphocyanogen. Accordingly, the addition of more iron salt also gives a deeper colour. The curve expressing the results of this experiment was a regular continuation of the curve formerly mentioned; and neither of them exhibited any of those sudden transitions which the experiments of Bunsen and Debus present. Diagrams exhibiting curves of the gallate and meconate of iron were also exhibited. Various experiments were then performed, showing the alteration in the resulting colour upon any change of any of the elements in the primary experiment; for instance, the substitution of other acids for the nitric acid, or of other bases for the potash. On the addition of a colourless salt to a coloured one, there results a diminution of the colour greater than the mere dilution would have produced, as was exemplified in the cases of the red sulphocyanide of iron mixed with sulphate of potash, and of the scarlet bromide of gold mixed with chloride of potassium. The lecturer accordingly drew the conclusion that when two salts mix without precipitation or volatilization, the acids and bases frequently, if not universally, arrange themselves according to some definite proportion; and that this depends on the relative quantity of the two salts, as well as upon the proper affinities of the substances composing them. He was unable then to enter upon the influence of heat, or of dilution in certain cases, or to add any remarks connected with double salts, or with other metals, or upon certain practical applications of these views in chemical and physiological science.

The fact that we very frequently find the double decomposition of a salt to be *complete*, the *whole* of one of its constituents being precipitated, was shown to be easily explained on the principles of Berthollet. Thus, for instance, when chromate of potash and nitrate of silver are mixed, at the first moment a division will take place producing four salts, but one of these — the chromate of silver, is thrown down at once as a precipitate, and thus put out of the field of action. Another division of the acids with the bases must take place, producing of course more of the insoluble chromate, and so on till at length the whole of the silver is removed. And that this is really what does take place is rendered almost certain by the fact that wherever by an interchange of acids and bases a precipitate can be produced, that precipitate does form; and, if the substance be perfectly insoluble, the whole is thrown down; this occurring in opposition to all rules of "affinity," and to all tables that Bergmann, or any other chemist, ever did or could construct.

The volatility of one of the products acts in the same manner as insolubility, as is exemplified in the decomposition of carbonates by any other acid. Crystallization also is but another phase of the same phenomenon. An experiment was exhibited in illustration of this. Dilute solutions of nitrate of lime, and sulphate of soda, were mixed at the ordinary temperature without producing any separation of solid matter; but they were so proportioned that upon heating the mixture, the crystallization of some sulphate of lime was determined, and when once this had commenced, it progressed rapidly; resembling in that respect the ordinary phenomena of precipitation. If in a double decomposition a far larger quantity of a sparingly soluble salt be produced at the first moment than the water can dissolve, the crystals will be formed rapidly and will accordingly be very small in size; but should there be formed at once only just sufficient to determine a separation in the solid form, the crystals will grow gradually, and will often attain a large size. This was exemplified on the mixture of nitrate of silver with the sulphates of copper and of potash respectively.

It is possible that the law of Berthollet may not be universally applicable; yet the present advanced state of science shows that not only is there, as Bergmann insisted, a true chemical affinity, that is—a preference of one substance to combine with a certain other substance instead of a third,—but, in a great number of instances at least, this substance will combine with both according to certain proportions, whenever the whole of the affinities can be brought into play at the same time.

[J. H. G.]

Royal Institution of Great Britain.

1854.

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[J. H. G.]

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, May 4, 1855.

Sir Charles Fellows, Vice-President, in the Chair.

Dr. J. H. Gladstone, F.R.S. M.R.I.

On Gunpowder, and its substitutes.

The object of the speaker was to return an answer to a question which had of late been frequently proposed to him, and no doubt to other chemists also :—" Cannot you now invent something much better than gunpowder? Are not some of your fulminating compounds much more powerful ? Why should we still be using a substance which was discovered long before chemistry was a science ? " Dr. Gladstone stated that some of his friends had considered him peculiarly qualified to give a reply to the query, since he had analyzed in turn the most terrible explosives with which modern science has made us acquainted ; yet he confessed he laboured under a disadvantage in having no practical acquaintance with gunnery, nor even with those experiments by which the propulsive force of different explosives is tested. He could give no categorical answer to the proposed inquiry. He could point to no substance, and say of it—" For use in fire-arms this is decidedly superior to gunpowder ;" nor was he willing to say—" No ; it is beyond the power of our science to invent anything better." He was desirous of laying before the audience some of the principles upon which a judgment might be formed ; of indicating the manner of investigation, as much as the results already arrived at.

In so doing he glanced first, in a cursory manner, at the various kinds of explosives with which chemists are acquainted. Any great and sudden increase of volume may give rise to the phenomena designated explosion ; but such great and sudden increase never takes place by the mere dilatation of a solid or liquid body : it is always necessary that gases should be formed. The simplest form of explosion is when a liquid is suddenly converted into a gas either by the removal of pressure, or by the bursting of the vessel in which

it was contained, as illustrated by the common "candle-cracker."
The enormous expansion of a gas by the removal of pressure is
taken advantage of for the projection of missiles in the air-gun,
and in Perkins's steam-gun. In these cases there is no chemical
change ; but usually an explosion is the result of a rapid chemical
action between the different constituents of a mixture, or chemical
compound, by which substances are produced that occupy a very
much larger space than the original combination did. Such an
explosion is always attended with heat, and generally with light and
noise. The substance exploded may be a mixture of two or more
gases : for instance, if the fire-damp of the mines be set fire to in
the air, it burns quietly with a luminous flame ; if, however, it be
previously mixed with air, on being ignited the flame passes instantly
throughout the whole mass ; and if mixed with twice its volume of
oxygen, this takes place with great violence, and a loud report.
One atom of the carburetted hydrogen combines with four atoms
of oxygen, to form carbonic acid and water. In this case, however,
the gases produced by the explosion would actually have occupied
less space than the original mixed gases, and a positive contraction
would have ensued, had it not been for the high temperature at
which they were formed. In order to obtain very great expansion
we must not start with a gaseous mixture. Solid or liquid oxygen
is a desideratum, but it can be procured in that condition only when
in a state of combination. There are several salts which contain a
large quantity of this element, and which give it up with great facility
—the nitrates and chlorates of potash or soda, for instance ; and these
salts contain also another element, which when free assumes a gaseous
condition, even at ordinary temperatures.

Dr. Gladstone then proceeded to show the violent combustion
that ensued when wood was thrown into one of these salts in a fused
condition, and to demonstrate the still greater effects that resulted
when the salt and the combustible had been previously mixed. He
then rapidly described the manufacture of gunpowder from nitre,
charcoal, and sulphur, and the different proportions of the three
ingredients that are employed in different countries. In exploding,
gunpowder produces carbonic acid and nitrogen gases, and sulphuret
of potassium, which is also dissipated by the great heat evolved, and
if it reach the air is converted into sulphate of potash, giving rise
to the white smoke that follows the explosion. Beside these gases
some others are always produced in small and varying quantity.
By burning a fuse under water these gases were exhibited. It is
supposed that, at the moment of explosion, the heated gases occupy
fully two thousand times the volume of the original powder. By
mixing different combustibles with nitre various effects may be
produced on explosion ; sometimes the light, sometimes the heat,
and sometimes the noise being the most remarkable. When nitre
was an article of scarcity in France, the French chemists made
many experiments with a mixture of chlorate of potash, charcoal,

and sulphur; but this compound, though a good explosive, has several disadvantages, which have prevented its ever coming into extensive use. A white gunpowder has more recently been prepared by mixing chlorate of potash with yellow prussiate of potash and sugar.

The explosives hitherto described are all mixtures. There exist substances which contain all the elements of combustion within themselves, and which require only a slight elevation of temperature, or a smart blow, to alter their state of chemical combination, and suddenly to produce gaseous bodies in large quantity. Pre-eminent among these is Gun-cotton: a substance formed by immersing cotton in a mixture of nitric and sulphuric acids. It is generally allowed now that this compound consists of lignine, $C_{24} H_{20} O_{20}$, in which a portion of the hydrogen has been replaced by NO_4; difference of opinion exists as to the amount so displaced, but Dr. Gladstone had found it to be five atoms in the most explosive gun-cotton, three in that of inferior quality, which he designated cotton-xyloidine. The most explosive compound produces a sudden flash, but no smoke or loud noise, and leaves no residue whatever. Hydrocyanic acid is among the resulting gases.—Nitroglycerine, a liquid produced in a similar manner from glycerine, is of so explosive a nature, that if a single drop be struck by a hammer on an anvil it gives rise to a deafening report. Its composition is $C_6 H_5 3 (NO_4) O_6$. Similar to this is nitromannite, which also explodes on percussion. Several other simple nitric acid substitution products are also capable of explosion; and so are certain salts of organic acids, which are analogous in their constitution; for instance, carbazotate of potash. Fulminating mercury and silver are also salts of an organic acid, the fulminic, which contains both oxygen and nitrogen. They explode, as is well known, by percussion, and with extreme violence. There are, however, certain detonating compounds, which contain no oxygen, nor any other supporter of combustion, but which are easily caused to undergo an internal change, and to resolve themselves into gaseous products. The most remarkable of these are certain substitution products of ammonia—the so-called ammoniurets of gold and other noble metals, and the so-called iodide and chloride of nitrogen. The iodide is a black powder, which when dry will explode on the slightest touch of a hard substance, and even sometimes by a sudden concussion of the air near it. Its composition had been examined by the speaker, and found to be always $N H I_2$. The chloride is a still more dangerous substance, since it explodes with the greatest facility under water. It is an oily liquid, discovered simultaneously in 1811, by M. Dulong, in France, and by a young English chemist, Mr. Burton, of Tonbridge. Dr. Gladstone's analyses gave as its composition $N_2 H Cl_5$.

The qualities requisite to render an explosive practically useful were then considered. This depends, of course, upon the purpose to which the explosive is to be applied. If it be merely for the

production of an instantaneous flame in order to ignite some other body, those compounds which are exploded by percussion have a great advantage.—Percussion caps of various kinds were exhibited —those intended for muskets being filled with a mixture of equal parts of fulminating mercury and chlorate of potash, fixed by a varnish; those made use of for cannon, being charged with two parts of chlorate of potash, two of native sulphuret of antimony, and one of powdered glass, which last appears to be practically a beneficial ingredient, although it takes no part in the chemical action. Caps made of fulminating mercury and collodion, bronzed over, were also shown.—Explosives, however, are generally intended for the projection of missiles, or for blasting. For either of these purposes propulsive force is the grand requisite. Now most of the compounds previously described explode too rapidly, and produce a very powerful local effect. If employed in fire-arms they would tear or strain the gun, and not propel the ball any great distance. Gunpowder, if tightly compressed, as in a fuse, or a port-fire, burns comparatively slowly; the necessary rapidity of explosion is given to it by granulation; and this can be modified according as the different purposes for which it is manufactured require. Supposing an explosive to have the necessary propulsive power, a very important quality is safety—safety in the process of manufacture, and in its subsequent keeping and handling. This practically excludes the use of all those compounds which are exploded by a blow. Gunpowder requires a temperature of 600° Fah. to ignite it; and this gives it a great advantage over gun-cotton, which is fired by a heat not much exceeding that of boiling water.—The comparative difficulty of exploding gunpowder was exhibited by setting fire to some ether round about a portion of it, which remained unaffected in the middle of the large flame; and by igniting a piece of gun-cotton without firing the little heap of powder on which it rested. Gunpowder may even be sprinkled on the top of gun-cotton, and the latter may be exploded, and cause the scattering of the black grains unaltered.—It is a desideratum that the explosive should not be injured by wetting. In this respect gunpowder fails, while gun-cotton, and several of the substances previously mentioned, suffer no injury by being soaked in water and dried again. Good gunpowder, however, is not materially affected by the ordinary damp of the atmosphere. Nitrate of soda, though it contains a much larger amount by weight of gas-forming constituents, cannot be substituted for nitrate of potash in the manufacture of gunpowder, partly because the resulting mixture is hygroscopic.—The complete combustion of an explosive is another desideratum. In firing cannon, a considerable portion of the charge of gunpowder is always lost, by being blown out unburnt; but this is the case to a much greater extent with gun-cotton, as was experimentally demonstrated. It is important also in respect to fire-arms that the products of combustion should not foul or corrode the piece.

Gunpowder leaves a considerable residuum, which has to be sponged out afterwards, but it is an alkaline salt, and has little effect upon metal.   Gun-cotton, on the contrary, leaves no residuum; but the piece remains filled with the highly corrosive red nitrous fumes which have an acid reaction.   Cheapness is, of course, an important element in comparing the practical value of different explosives; but the calculation must be made not according to the weight, but according to the propulsive force of the various substances.

This review of the qualities requisite in an explosive shows that gunpowder is admirably suited to such a purpose, on account of its great propulsive power with little local strain, its great safety, both in manufacture and in use, and its cheapness.   It has two disadvantages; its being spoilt if wetted, and its leaving after explosion a quantity of solid matter.   It is evident, that most of the fearfully explosive substances, with which chemistry has made us acquainted, are perfectly inapplicable to the projection of balls. Mixtures containing chlorate of potash, though good in some respects, are dangerous.   Gun-cotton is the only substance that puts forth just now any great pretensions, as a substitute for gunpowder; its propulsive force is somewhere about three times that of an equal weight of powder, and it has some other advantages, coupled however with serious disadvantages.   The Austrian government has lately put it very fully to the test of experiment; and that they have been to some extent satisfied of its value, is attested by the fact, that a considerable number of cannon, of great thickness of metal about the breach, have been formed expressly with the object of employing it.

It is said to be a modification of gun-cotton which is used; and the speaker thought it most probably was either a lower substitution product of cotton, or a mixture of ordinary gun-cotton with some other substance.   In England, experiments have sometimes been made with this material, and it is said to have been employed with advantage for filling shells at the siege of Moultan; but on account of the many accidents that have occurred with it, it finds little favour at present with our military authorities.

Dr. Gladstone concluded, by stating, that though he considered war under any circumstances to be a fearful evil, yet he wished he could point out a still more efficient explosive than gunpowder; for he believed that to render war a more certain game tended to indispose men to engage in it.   He was glad to be able to state, that the Government had lately organized the means of examining the merits of every suggested improvement, and that the appointed parties were now actively engaged in the investigation.   At present there appear two improvements in the art of war, in which chemical science may be of service: the one in making shells, which shall burst upon striking—about which there is no chemical difficulty; the other in charging shells with substances that will give forth quantities of poisonous gas; a subject which has lately attracted

much attention. It is to be hoped, that not only mechanical, but also chemical science, will soon furnish us with improvements on the present means of carrying on the war in which we are now engaged.

[J. H. G.]
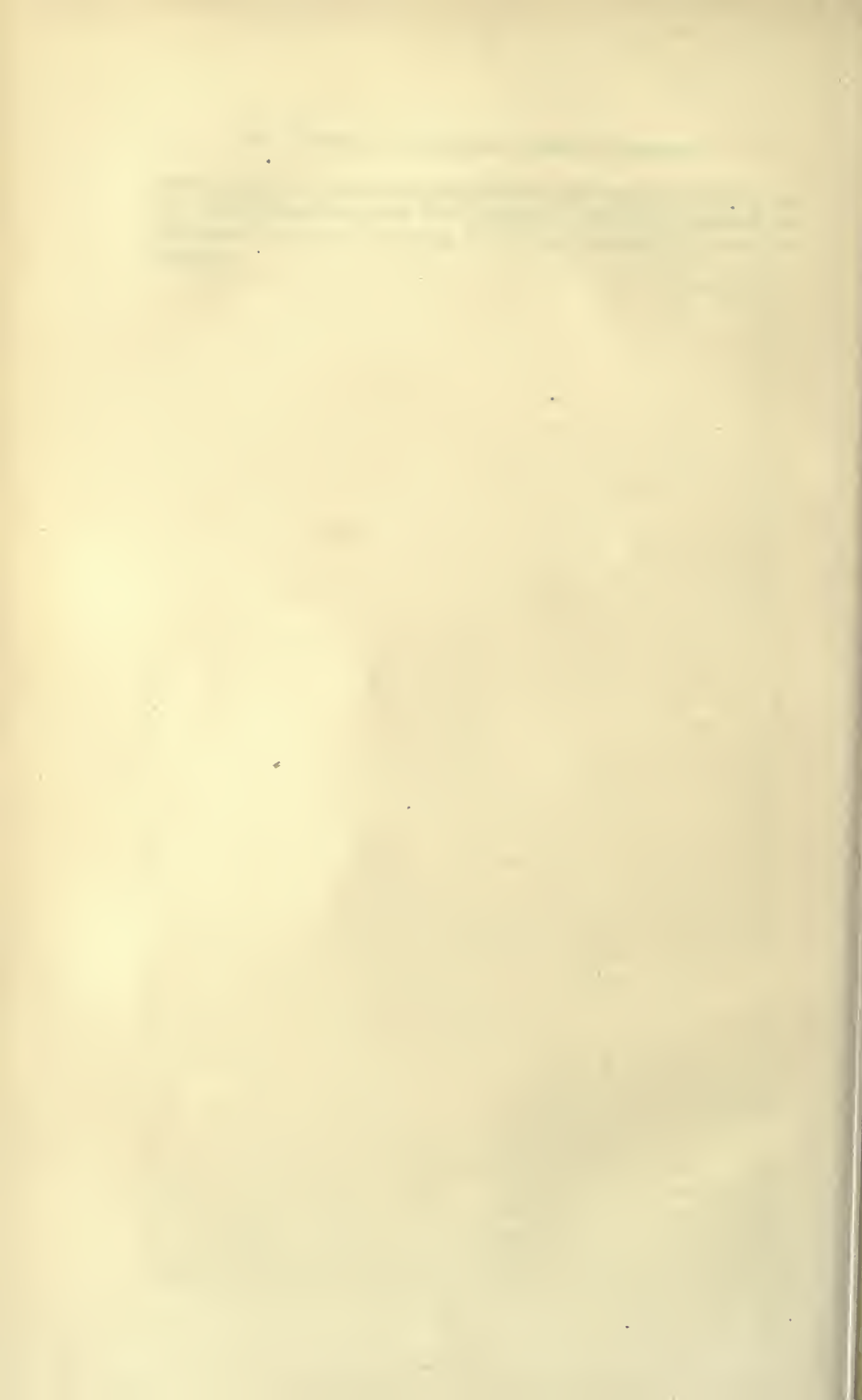
Some Experiments illustrative of the Reciprocal Decomposition of Salts.

By J. H. GLADSTONE, Ph.D., F.R.S.

AMONG the conclusions arrived at by me in a paper published in the "Philosophical Transactions" of last year, were the following :—

"Where two or more binary compounds are mixed under such circumstances that all the resulting bodies are free to act and react, each electro-positive element arranges itself in combination with each electro-negative element in certain constant proportions."

"These proportions are not merely the resultant of the various strengths of affinity of the several substances for one another, but are dependent also on the mass of each of the substances in the mixture."

My impression is that these laws are of universal application; but this can be established only by the observation of a large number of varied instances in which they hold good, and by the investigation and explanation of every supposed exception.

The present paper contains the account of some reactions bearing upon the subject, which are of value, either from the experiments having been performed with elements hitherto untried, or from some novelty in the mode of observation. Every difficulty which, to my knowledge, has been proposed by others, or which has occurred to my own mind, has been examined, and is here commented on.

Chromium Salts.—The soluble chromic salts have very remarkable optical properties. Their colour, by transmitted light, depends not only for its depth, but for its very character, upon the amount of salt which the ray has traversed in the solution. If the solution be weak, or if only a thin stratum be seen, it appears green; if a stronger solution or a thicker stratum, it appears red. As these two colours are complementary, or nearly so, the red on dilution passes into the green, not by a strictly speaking intermediate shade, but by a kind of brown or neutral tint. Now though, as far as I am aware, this description applies to all the soluble chromic salts, the amount of oxide requisite to give the red appearance depends greatly upon the acid with which it is combined. Thus, if equal portions of chromic oxide be dissolved in acetic and in sulphuric acids, it is very easy to arrange it so that, when viewed through

glasses of equal capacity, the acetate appears red, and the sulphate green. If now to the red acetate a few drops of sulphuric acid be added, it passes through the neutral tint to the green colour; or if contrariwise, a little glacial acetic acid be added to the green sulphate, it assumes the reddish hue.

It is interesting to observe this change of colour by means of a prism. If a luminous object be viewed through any solution of a chromic salt, it exhibits two images, the one red, and the other green, fringed with blue. The relative intensity of colour of these two images differs with the amount of salt looked through, and with the character of the electro-negative element. On the addition of acetic acid, the red image becomes comparatively brighter and brighter, while the green image pales; and contrariwise, on the addition of hydrochloric or sulphuric acid, the green image becomes comparatively more and more distinct, while the red one fades. Again, if a solution of the acetate be seen through the sides of a wedge-shaped glass vessel, the stratum near the angle will appear green, that near the broad end red, while about a certain line neither colour will preponderate. On the addition of sulphuric acid this line advances towards the broad end, while acetic acid brings it again nearer the angle.

Ferrous Salts.—The mutual displacement of sulphuric and acetic acids may be also rendered visible by means of the protoxide of iron. If to a green solution of sulphate of iron a solution of acetate of potash be added, a brown colour is the result. If sulphuric acid be added to this, the pale colour is more or less restored; if an addition of acetate of potash be then made, the brown reappears. This may be repeated many times with the same solution.*

Cobalt Salts.—The sulphocyanide of cobalt in an anhydrous condition, like the chloride, is blue; but, unlike that salt, it retains its blue colour when dissolved in a little water. As the solution is diluted, it gradually assumes the red tint which characterises solutions of the compounds of this metal. If very strong solutions, containing corresponding equivalents of chloride of cobalt and sulphocyanide of potassium, be mixed, a blue colour makes its appearance, showing the formation of sulphocyanide of cobalt. But that the double decomposition has not been complete, may be made evident by carefully diluting the blue mixture with water till it has become distinctly red, and dividing it into two parts. If to

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* This experiment was suggested by a remark in Professor Miller's Chapter on "Some Circumstances which Modify the Operations of Chemical Affinity," in his "Elements of Chemistry, Theoretical and Practical," vol. ii.

the one portion some of the very strong solution of sulphocyanide of potassium be added, the blue colour is restored; on the addition of more water, it disappears; and this may be repeated a number of times, until ten or twelve equivalents of sulphocyanide of potassium has been added to one of chloride of cobalt. If, inversely, to the other portion of the original mixture chloride of cobalt be added, that substance also produces a blue colour, which may be likewise caused to become red, or to reappear many times, by the successive addition of water or chloride of cobalt.

Chromates.—During the past year the " Journal de Pharmacie et Chimie"[*] has published an extract, in which Margueritte proves that " chromic acid can displace hydrochloric, nitric, and even sulphuric acids, and take away from them a part of the base to which they are united, whether that base be strong or weak." We all know that these acids are capable of displacing chromic acid; indeed, the same investigator has shown that even boracic and carbonic acids will decompose bichromate of potash. By a method of observation almost identical with that adopted by myself, he found that the addition of such salts as chloride of potassium, or the nitrate or sulphate of potash or ammonia, to a solution of the red bichromate of potash, caused the production of yellow monochromate. Such experiments, he conceives, lend support to his view of " the partition of a base between the two acids, when any acid is added to any saline solution;" which is identical with the law of Berthollet, or rather is included in the more general expression.

One objection, however, may be taken to this conclusion from Margueritte's experiments. It may be contended that the salt added merely displaces the one equivalent of chromic acid in the bichromate of potash, and that, in fact, the reaction is according to the formula:

$$KO,2CrO_3 + KO,SO_3 = 2(KO,CrO_3) + SO_3.$$
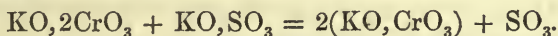
Indeed, this idea seems to have been in the mind of Schweizer, in a paper published a few months ago on these reactions of chromic acid.[†] The point seemed to admit of easy determination, for if the decomposition really take place in that manner, the production of the yellow colour will be perfect when single equivalents of the two salts are mixed, and no subsequent addition of sulphate of potash will lighten the tint. On trying the experiment it was found to be otherwise. The addition of one equivalent of sulphate

* J. Pharm. [3] xxvii. 21.   † J. pr. Chem. lxv. 173.

of potash to one of bichromate of potash caused certainly a diminu-
tion of the red tint; but successive additions of the sulphate to the
previous mixture caused the yellow to become more and more
decided.   Hence it may be concluded, that the mixture of single
equivalents contains both bichromate and monochromate of potash,
besides sulphuric acid and sulphate of potash, and possibly free
chromic acid.

Copper Salts.—M. Alvaro Reynoso has recently published
some "facts relating to the double decomposition of salts."[*]   By
taking advantage of the power of glucose to reduce the acetate of
copper, he finds that when acetates of the alkalies, earths, or metals,
are mixed with the nitrate or sulphate of copper, the acetate of
that metal is produced.   This is, so far, in accordance with the law
of Berthollet; but whether the decomposition be complete or
not does not appear from his experiments, though the action of
mass is very evident in some of them.   One remark, however,
presents some difficulty.   He observed that acetate of copper,
mixed with ferric nitrate or sulphate, loses the property of being
reduced by glucose.   This I have repeated quantitatively.   Solu-
tions of acetate of copper and nitrate of iron were prepared of
known strength; they were mixed together in certain proportions,
with the addition of glucose, and boiled.

	Salts mixed with glucose.						Result.
	Acetate of copper	.	.	.	.	.	Immediate decomposition.
3 eq.	„	„	+ 1	eq. ferric nitrate			Deposit after boiling.
3 eq.	„	„	+ 1·5 eq.	„	„		Deposit after long boiling.
3 eq.	„	„	+ 2	eq.	„	„	Deposit after very long boiling.

From this it may be concluded that $3(CuO,AcO_3) + Fe_2O_3,3NO_5$
do not become wholly $3(CuO,NO_5) + Fe_2O_3,3AcO_3$.   This also was
confirmed by the colour: for the mixture of two equivalents of the
ferric nitrate with three of acetate of copper was deeper in tint
than when the salts were mixed in the proportions merely necessary
for the above double decomposition.

This reaction, then, instead of militating against the conclusion
illustrated in this paper, serves to support it.

In the "Comptes rendus" for last year, there also appear
papers by Tissier[†] and Bineau,[‡] narrating experiments con-
firmatory of the views arrived at by myself and other investigators;
but they call for no further remark.

[*] Compt. rend. xli. 278.
[†] "On some Facts relating to Double Decomposition," p. 362.
[‡] "On the Solubility of certain Metallic Oxides and Earthy Carbonates, and on
some Reactions produced by their Solutions," p. 509.

EVIDENCE FROM CIRCULAR POLARISATION.

Camphorates.—It was an early idea of mine that the effect of chemical affinity among substances in solution might be tested by means of circular polarisation; yet the evident intricacies of the subject deterred me from making any experiments: nor, indeed, did I see a case suited to my purposes. M. Bouchardat,[*] however, has announced that camphoric acid dissolved in alcohol causes a right-handed rotation; and that when it is saturated with a base, the rotation is considerably diminished, but is restored again on the supersaturation of the base by another acid. Yet, if I understand his experiments rightly, it appears that in the latter case the original amount of rotation is not quite obtained. Thus he gives the numbers:—

Camphoric acid	12° R.
The same, saturated with soda	7° R.
The same, supersaturated with hydrochloric acid	11° R.
Camphoric acid	22° R.
The same, saturated with ammonia	12° R.
The same, supersaturated with hydrochloric acid	21° R.

Are we wrong in deducing from these results that the hydrochloric acid did not completely decompose the alkaline camphorates first formed?

SALTS DISSOLVED IN ACIDS.

Sulphate of Baryta.—Within these last few months, no less than four papers have appeared, in which the solubility of sulphate of baryta in hydrochloric acid is discussed. Professor Rose,[†] Mr. Crace Calvert,[‡] Dr. Noad,[§] and Messrs. Nicholson and D. Price,[||] have shown by independent experiments, not only that sulphate of baryta is, to a certain extent, soluble in these acids, but that the amount dissolved is most materially diminished by the presence of an excess of baryta salt. Rose states that the solution of pure sulphate of baryta in either of the above-mentioned acids gives a small precipitate when treated with either chloride of barium or dilute sulphuric acid. He says, " It is a striking circumstance that the presence of the dissolved sulphate of baryta is indicated by both these reagents," and he concludes that the salt in question " is less soluble in sulphuric acid and in chloride of barium than in hydrochloric acid and nitric acid." Yet the great

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* Compt. rend. xxviii. 319.

† Pogg. Ann. xcv. 108. § Chem. Soc. Qu. J. ix. 15.
‡ Proc. Roy. Soc. vii. 532. || Phil. Mag. 1856 [4], xi. 169.

analytical chemist can scarcely offer this as a satisfactory explana-
tion; for, in the experiment, the acid solvent still remains, capable,
of course, of exerting its former power. Indeed, the next sentence
shows the insufficiency of the reason; for Rose remarks that sul-
phate of baryta does not separate from the acid solution by means
of water, although it is assuredly less soluble in water than in
hydrochloric or nitric acids.

However, this " striking circumstance" is precisely what might
be expected if the law of reciprocal decomposition, as quoted above,
be true. If sulphate of baryta in excess be treated with an acid—
say nitric—that portion which is brought into solution will suffer
partial decomposition, and a solution will eventually result, con-
taining as much sulphate of baryta as the free acid is capable of
dissolving, and as much nitrate of baryta and sulphuric acid as is
capable of counterbalancing the two other bodies. Such being
the case, the addition of either sulphuric acid or baryta salt will
disturb the equilibrium, with the production of fresh sulphate of
baryta, which must precipitate, seeing that the acid solution was
previously saturated.

Sulphate of Strontia.—Rose observed the same with sulphate of
strontia as he did with sulphate of baryta. Of course it is capable
of the same explanation.

Sulphate of Lime.—On examining a solution of sulphate of lime
in hydrochloric acid, Rose observed that a precipitate formed when
it was treated with sulphuric acid, but not when it was treated with
a solution of chloride of calcium. That this precipitation by sul-
phuric acid is incapable of the explanation offered by him in the
case of sulphate of baryta, he shows by the observation that " a
concentrated solution of sulphate of lime in water is *not* precipitated
by sulphuric acid." But the non-precipitation by chloride of cal-
cium presented a difficulty to my explanation.

Two possible reasons suggested themselves to me, and, for-
tunately, each was capable of being put to the test of experiment.
It might be that one equivalent of sulphate of lime is capable of
being dissolved (or decomposed) by not more than one equivalent
of hydrochloric acid. In that case, the formation of any amount of
sulphate of lime from chloride of calcium would set free an equiva-
lent amount of hydrochloric acid, which would keep it in solution.
It was found, however, that one equivalent of sulphate of lime
required three equivalents of hydrochloric acid (somewhat dilute)
at the ordinary temperature to dissolve it.

The other supposition was that chloride of calcium might itself

exert a solvent action on sulphate of lime; but this was found not to be the case.

The only supposition, then, that seemed possible, if my view were correct, was that such a small amount of additional sulphate of lime was formed that it was soluble in the water which was added at the same time as the chloride of calcium. This, happily, was also capable of being put to the proof by employing a very concentrated solution of the chloride. On doing so, a cloudiness at once appeared, which soon became a decided precipitate of crystallised sulphate of lime.

These reactions are all explicable on the supposition that when sulphate of lime is dissolved in hydrochloric acid, nearly (but not quite) all is converted into chloride of calcium.

Though sulphate of lime is not rendered more soluble in water by the presence of chloride of calcium, it does dissolve more freely when *other* chlorides are present. A. Vogel* has shown this in reference to chloride of ammonium and common salt: I have tried the experiment with four metallic chlorides—those of zinc, copper, iron, and chromium, and have found it to be the case with each. Now this is precisely what might be expected, supposing the two salts to suffer reciprocal decomposition, with the conversion of more or less of the sulphate of lime into the very soluble chloride. Vogel observes that when the solution in chloride of ammonium is evaporated to dryness, and heated to redness, pure sulphate of lime remains; and this has been employed as an argument against Berthollet's views: yet when we reflect how very volatile is the ammoniacal chloride, while the sulphate is not volatilised without decomposition, we shall see that no other final result could be obtained.

Sulphate of Lead.—Wackenroder† states that sulphate of lead dissolved in nitric acid is precipitable by sulphuric acid. I find that such a solution gives a precipitate also when treated with nitrate of lead.

This case is mentioned, because a statement of Wackenroder has been employed as an argument against the Berthollian hypothesis. The German chemist says that sulphuric acid, in large quantity, precipitates the sulphate of lead *completely*, notwithstanding the presence of the nitric acid. Yet, farther on in his paper, he proves that the said precipitation is *not* absolutely complete, and it is evident that, by employing the word " *vollständig*,"

* J. pr. Chem. xi. 196.   † Ann. Ch. Pharm. xli. 316.

he merely meant to say that the action was sufficiently perfect for ordinary analytical purposes.

Sulphate of Mercury.—W a c k e n r o d e r also shows that the insoluble sulphate of mercury dissolved in nitric acid is precipitable by sulphuric acid.

Oxalate of Lime.—In order to vary these observations by experiments on other salts than sulphates, a saturated solution of oxalate of lime in dilute hydrochloric acid was prepared. On the addition of oxalic acid, a white precipitate after a while made its appearance ; and on the addition of chloride of calcium to another portion, a precisely similar result ensued.

Chloride of Lead.—Dilute nitric acid was saturated with chloride of lead, and divided into two portions. To the one, hydrochloric acid was added, which caused an instantaneous precipitate ; to the other, nitrate of lead was added, and, after some time, long crystals of chloride of lead formed.

Phosphate of Iron.—Hitherto the fact, that when a salt insoluble, or slightly soluble, in water, has been dissolved in an aqueous solution of any acid, the base divides itself in certain proportions between the two acids, has been deduced merely from the reactions of which such a solution is capable. It seemed desirable to prove this, if possible, by direct ocular demonstration. Phosphate of iron appeared to offer an opportunity of doing so. It is white in the solid state, but dissolves in hydrochloric acid with an orange colour. Now, if this colour be due to ferric chloride, we have a means of judging whether the whole of the iron be in that condition. Accordingly, some dilute hydrochloric acid was saturated with ferric phosphate. A portion was found to contain the same amount of colour as an aqueous solution of 0·067 grm. of ferric chloride ; but the acid liquid itself consisted of 0·585 grm. of ferric phosphate dissolved in 0·477 grm. of real hydrochloric acid. Evidently, therefore, the whole of the iron was not in the state of chloride ; indeed, supposing the ferric phosphate to have been of the usual composition, $2(Fe_2O_3)3PO_5$, the amounts of iron in the two equi-tinted solutions were—

In the solution containing both phosphoric
and hydrochloric acids .   .   . 0·164 grm. Fe.
In the solution of pure ferric chloride . 0·023 „   „

Hence it would appear, that when ferric phosphate is dissolved in the smallest possible amount of hydrochloric acid, only one-seventh part is converted into the chloride.

It is here assumed that the ferric phosphate, which is white in

its pure state, has no colour of its own when dissolved.   In other ways, also, the above numbers may not be very exact; yet one thing is certainly proved,—that when phosphate of iron is dissolved in a minimum of hydrochloric acid, it is not wholly, or principally, converted into the chloride.

It may be expected that if a considerable amount of the iron still remain as phosphate, the addition of more hydrochloric acid will decompose more or less of this, and increase the colour.   Such was found to be actually the case.

These experiments could not be advantageously performed by looking horizontally through the solution, for the golden tint of the ferric chloride is very little altered by dilution.   A comparison, however, is easily made by looking perpendicularly through the solutions contained in glasses of uniform diameter.

The addition of phosphoric acid to the acid solution of ferric phosphate gave an immediate flocculent precipitate.   I failed, however, to obtain a precipitate on the addition of ferric chloride.   This is the first exception to the general inference that if a salt AB dissolve in an acid CD, the addition of either AD or CB will cause the production of more AB than the acid can keep in solution; yet when the peculiarity attending the saturating power of phosphoric acid is considered, it will probably present no great difficulty to the reception of that as a general law.

REPUTED EXCEPTIONS.

Beside the *primâ facie* difficulties already discussed, other reactions have been urged against the general conclusions adopted by me, and these claim a careful examination.

Cyanide of Mercury.— Reactions of an apparently anomalous character take place among mercury salts: thus, the cyanide affords two instances where an insoluble compound does not form, although, from the reciprocal decomposition of the compounds mixed together, it might be expected to make its appearance.   When the cyanide of mercury is treated with potash in solution, the insoluble oxide does not precipitate; and when mixed with nitrate of silver it produces none of the insoluble cyanide of that metal.

The first of these apparent anomalies depends perhaps on the formation of the well-known oxycyanide of mercury, which is a ternary compound soluble in water.   The annexed formula represents this decomposition:—

$$2HgCy + KO = Hg_2CyO + KCy$$
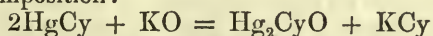
though such a mixture may contain, I apprehend, simultaneously all the four substances, besides the double cyanide of mercury and potassium.

As to the second anomaly, cyanide of mercury forms a soluble crystalline double salt with nitrate of silver, which has been analysed by Wöhler,* who assigns to it the composititition $AgO, NO_5, 2HgCy, 4HO$. But were we to overlook this, the decomposition might be supposed to take place thus :—

$$3(HgCy) + 3(AgO, NO_5) = HgCy, HgO, NO_5 + 2Ag\,Cy,$$
$$AgO, NO_5 + HgO, NO_5$$
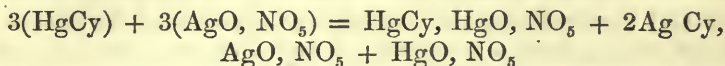
all of which, beside the original salts, are soluble in water.

Boracic Acid.—The objections most frequently urged are founded on the behaviour of boracic acid. It is contended that this acid has no power to decompose sulphate of potash, and that borax is completely decomposed by an equivalent of sulphuric acid. I have already shown† that the non-alteration in colour of litmus does not prove this, but I have in vain sought for some property which would enable us to decide what actually does take place in the above-mentioned mixtures. Indications, however, have been obtained where boracic acid was mixed with another sulphate, and also where it was mixed with another potash salt ; and in each of these cases it was found capable of effecting some decomposition.

The borate of quinine in solution, like the hydrochlorate, is non-fluorescent, or nearly so. If boracic acid be added to a neutral, and consequently non-fluorescent solution of sulphate of quinine, it immediately exhibits the beautiful surface blue, just as though a drop of hydrochloric acid had been added, and doubtless from the same cause—the formation of some bisulphate through the abstraction of some of the quinine by the other acid.‡ The addition of a very large quantity of boracic acid appeared to diminish the colour, and consequently to indicate the decomposition of the bisulphate; but I certainly never succeeded in destroying the fluorescence, as is easily done when the powerful hydracids are employed.

Three solutions were prepared—the first of boracic acid, the second of pure nitrate of potash, the third of a mixture of the two; and they were digested for some time with metallic copper, after which the solutions were tested with ammonia in excess. The first showed absolutely no blue, the second only a faint trace, while in the third the blue colour was very decided. From this it may be inferred that the boracic acid had displaced some of the nitric acid, which in its turn had attacked the copper. The quantity of copper dissolved must, however, have been exceedingly small.

* Pogg. Ann. i. 231.   † Phil. Trans. 1855, 220.
‡ See Stokes's paper, Phil. Trans. 1852, 542 ; also, 1855, 210.

It has also been objected that boracic acid occasions no precipitate in a solution of nitrate of lime, although borate of lime is an insoluble salt. Now there are said to be compounds of boracic acid and lime, which are not insoluble in water: and, moreover, the production of borate of lime from the nitrate must liberate an equivalent amount of nitric acid, which of course will exert its own solvent power. But while the non-precipitation of a borate is evidently inconclusive as to what really happens in the mixture, it appeared to me that metallic copper would also in this case furnish an indication. The experiment was accordingly tried as with the potash salt, and it was found that the neutral nitrate of lime had no action on copper, while the mixture of nitrate of lime and boracic acid produced a solution which was rendered blue by ammonia, and during the digestion a gelatinous substance formed in small quantity about the shreds of copper.

It thus appears that boracic acid is able to displace other acids from their combinations, though but to a slight extent, in the cases just examined.

REGULAR PROGRESSIVE CHARACTER OF THE INFLUENCE OF MASS.

From the experiments detailed in the paper already referred to, I was led to the conclusion, that—" An alteration in the mass of any of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regular progressive ratio ; sudden transitions only occurring where a substance is present, which is capable of combining with another in more than one proportion." Yet there is one experiment recorded which appears to offer an exception, and to indicate changes of ratio somewhat similar to those observed by Bunsen and by Debus, in cases where the resulting compounds were not capable of reacting. This experiment is where a solution of oxalate of lime in hydrochloric acid was precipitated by the addition of acetate of potash or soda. The table drawn out, and the curves projected from the experiments, show considerable irregularities ; but as each experiment consists of six or eight separate observations, it was thought desirable to repeat the experiment, taking every precaution to ensure the observations being all made under the same circumstances.

Into each of ten glasses were poured 400 grain measures of a solution of oxalate of lime in hydrochloric acid. Different amounts of a solution of acetate of potash were mixed thoroughly with these, and the solutions were made up to the same bulk by the addition of water. After standing twenty-four hours, the resulting pre-

cipitates were washed the same number of times by suffusion and decantation ; they were then boiled with pure water, and collected.

Oxalate of lime in hydrochloric acid.		Acetate of potash added.		Oxalate of lime precipitated.	
400	gr. meas.	50	gr. meas.	0·015	grm.
400	,,	100	,,	0·049	,,
400	,,	150	,,	0·102	,,
400	,,	200	,,	0·136	,,
400	,,	250	,,	0·193	,,
400	,,	300	,,	0·278	,,
400	,,	350	,,	0·336	,,
400	,,	400	,,	0·350	,,
400	,,	500	,,	0·354	,,
400	,,	600	,,	0·354	,,

On the addition of potash to the filtrate from the last experiment of this series, a slight turbidity was produced, from the separation of oxalate of lime, showing that the whole of the hydrochloric acid had not even in that case been converted into chloride of potassium.

From the table it will be seen that a larger addition of acetate of potash caused a larger deposit of oxalate of lime, and that in a ratio which, though somewhat remarkable, was tolerably regular in its character. As it may be interesting to know the proportionate equivalents of the substances in each experiment, they are given in the annexed table. The initial 400 grain measures of acid solution contained 0·375 grm. of oxalate of lime, dissolved in 2·26 grms. of hydrochloric acid, nearly the proportion of 1 equiv. to 12 ; and each 100 grain measures of the acetate of potash solution contained 1·80 grm. of the anhydrous salt.

Oxalate of lime.		Hydrochloric acid.		Acetate of potash.		Oxalate of lime deposited.	
1	equiv.	12	equiv.	1·75	equiv.	0·04	equiv.
1	,,	12	,,	3·5	,,	0·12	,,
1	,,	12	,,	5·25	,,	0·27	,,
1	,,	12	,,	7·	,,	0·36	,,
1	,,	12	,,	8·75	,,	0·51	,,
1	,,	12	,,	10·5	,,	0·74	,,
1	,,	12	,,	12·25	,,	0·90	,,
1	,,	12	,,	14·	,,	0·93	,,
1	,,	12	,,	17·5	,,	0·95	,,
1	,,	12	,,	21·	,,	0·95	,,

The examination of these new substances, and of those reactions which appeared to be exceptional, tends therefore only to confirm the former conclusions. I propose to investigate, as they arise, any further objections founded on experiment.

ON THE

CHEMICAL ACTION OF WATER

ON

SOLUBLE SALTS.

By Dr. J. H. Gladstone, F.R.S.

In pursuing my researches on chemical affinity among substances in solution, it seemed desirable to ascertain, if possible, what specific chemical action water exerted on a salt. Unfortunately my experiments in this direction have not led to any such conclusive result as I had hoped; yet, during the course of the inquiry, many observations were made which I believe to be new, and some of which I think are not unworthy the notice of chemists.

In order to bring these observations clearly before the minds of others, it may be well to associate them with the leading trains of thought that presented themselves to my own mind during the investigation; and, as in a difficult discussion it is very necessary to examine the simpler before attempting the more complex phenomena, it will be wise to confine the attention first to simple salts, and indeed to begin by trying to ascertain what is the action of water on such a salt *before* it dissolves it.

Anhydrous salts will frequently absorb water, and still remain solid bodies, either amorphous or crystallized. In such a case, the water combined in the solid form is always in atomic relation with the salt itself. The language of chemists implies the general belief

that a certain number of equivalents of water are then simply added to the original salt; yet great heat is often evolved, and a change of colour frequently ensues.* I know of no reason to think that the water in such a case has been decomposed by the salt (whose composition may be expressed by the general formula MR), and that the resulting solid contains any such compound as MO,HR, though should any one choose to advance such a view he would not be wholly without arguments to support it.

These "hydrated" salts are usually, but not always, soluble in water. When solution does take place, those difficulties, as to their rational composition, of which we have already seen the commencement, increase; for there is now scope for more varied chemical actions, and consequently for a wider range of speculation. The water may act merely as a solvent; or it may unite without decomposition with the dissolved salt, becoming an integral part of it; or it may exert an action similar to what usually takes place when two binary compounds are united under such circumstances that all the resulting bodies are free to act and react, namely, that reciprocal decomposition ensues, each electro-positive element combining with each electro-negative one in certain proportions; or the ultimate result may be due to two or more of these modes of action in conjunction.

Usually when a "hydrated" salt is dissolved in a minimum of water, nothing is observable beyond a change in its state of aggregation, and the new physical properties, and the absorption of heat resulting from that. No change of colour, as far as I can find, ever ensues. A change in fluorescence may occur.† There is no atomic relation between the quantity of salt dissolved, and the quantity of water, indeed the ratio varies with the degree of temperature. Here we *seem* to have the simplest case of solution, such as we necessarily conceive when a salt dissolves in ether, or a fat in an essential oil.

When an anhydrous salt, which will not combine with water to produce a solid compound, dissolves in that liquid, the same phenomena usually present themselves, except that a change in colour

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* For a case in point, and some remarks on it, see my paper "On the Colour of Chloride of Copper in Different States of Hydration." Quart. Journ. Chem. Soc., viii, 211.

† As in the case of crystallized salts of uranium, which are much more fluorescent than their saturated solutions. See the paper of Prof. Stokes, Phil. Trans., 1852, 517. This observation, as every other quoted or reasoned on in this communication, has been verified by myself.

may occur; as in the case of red prussiate of potash, which gives a green saturated solution.

Sometimes, however, an evident decomposition ensues, the hydrogen and oxygen of the water combining each with one of the elements of the other binary compound, and the products of this action remaining uncombined. This is common among the compounds of the non-metallic bodies—as, for instance, the chlorides of phosphorus,—and is not unknown among what are more properly called salts, for instance chloride or nitrate of bismuth, or sulphate phosphate or citrate of ammonia. In such cases the decomposition makes itself manifest by the separation of the one resulting substance from the other. The bismuth salt treated with water forms an insoluble subsalt; the compound of ammonia with a polybasic acid gives off some of the volatile alkali when its solution is heated, while the liquid itself becomes acid. It is certain, however, that in the vast majority of cases of solutions of salts, no such interchange takes place, with the production of a new oxygen and a new hydrogen compound uncombined; if chloride of copper be dissolved, no oxide of copper, or subsalt, is precipitated, and no hydrochloric acid can be boiled off. Yet it has been contended that a haloid salt in dissolving ceases to be of the constitution MR, and becomes MO, HR; only that the two new products, instead of separating, form one compound body. When this theory was started, there was supposed to be a wide difference in the essential constitution of haloid and other salts; our views have now changed, and there seems to me now no logical grounds on which, if we consider a haloid salt in solution to be MO,HR, we can stop short and refuse to consider this as the general expression of any salt in solution.

I was unacquainted with any argument of weight in support of this hypothesis; yet, on the other hand, it had never been actually disproved. Analogy, too, led me to view it with some favour, for it seemed reasonable to suppose that water might act like hydrochloric acid, or a similar hydrogen compound, and that possibly an aqueous solution of a salt might resemble a solution of ferric phosphate in hydrochloric acid, which contains portions of both the original salt and the hydracid, mixed with ferric chloride and phosphoric acid.* The action of HO on MR would by analogy

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* See my paper, in the Quart. Journ. Chem. Soc., ix, 152. Of course water was present in the reaction alluded to there, but I have repeated it in absolute alcohol with a similar result.

result in a reciprocal decomposition, MO and HR being formed—either separate or in combination—while portions of the original HO and MR coexisted in the same solution.

But how was this to be decided? By all analogy it might be anticipated that by increasing the amount of HO more MR would be decomposed, just as the addition of more hydrochloric acid to a solution of ferric phosphate in that acid, produces more ferric chloride and heightens the colour. The action of water when added to a saturated solution of a salt becomes therefore a matter of peculiar interest.

That such an addition of water produces a decomposition is sometimes evident from the separation of a precipitate—and that in several different ways. Thus :—

Pentachloride of antimony, as is well known, though soluble in a small amount of water, is decomposed by a larger quantity, giving rise to hydrochloric acid, and an oxychloride of the composition $SbClO_2$, according to Peligot.

A strong solution of ferric sulphate, if diluted with water, deposits a subsalt, $3Fe_2O_3,SO_3 + 7HO$.*

The intensely blue solution of crystallized ammoniacal nitrate or sulphate of copper in a little water is perfectly clear, but on dilution it becomes turbid from the separation of a subsalt, the quadrobasic sulphate, while free ammonia is perceived in the solution.

Nitrate of bismuth, if slightly acid, dissolves in a little water, but forms a white precipitate, of varying composition, when this is poured into a larger quantity.

In all these cases, the amount of precipitate increases, within certain limits, with the amount of water added. The full action of the water also does not take place instantly. Yet it must be borne in mind that not one of these salts is of simple constitution after the type MR, and that the products of decomposition are never MO, but some new salt of complicated composition. There is this difference too between these cases and all those instances of reciprocal decomposition which are recorded in my paper "On the circumstances modifying the action of Chemical Affinity," that here a large amount of water, many equivalents in fact, is required before any trace of the insoluble compound is formed.

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* According to Scheerer, this is $2(3Fe_2O_2SO_3) + 9HO$, but the specimens analyzed by me contained more water.

That the addition of water to a saturated aqueous solution of a salt produces some chemical change is sometimes apparent from a change in colour. This phenomenon was closely examined.

It might be anticipated, *a priori*, that a certain amount of salt would have the same absorbent effect on a given number of rays of light, whether it were dissolved in much or in little water, and that, as the absorbent power of water is practically *nil*, it would appear to the eye of precisely the same depth and character of colour in the two cases. And this actually happens in the majority of instances; but, to perform the experiment, it was, of course, necessary to make the same quantity of light impinge upon the solution before and after dilution, and this required a special contrivance. Colourless cylindrical glasses of uniform diameter and of the same size were procured, and they were each closed at one end with a flat plate of glass. These were placed side by side in a wooden frame (something like that of an ordinary stereoscope), which was painted black within, and so made that it prevented any light from passing into the cylindrical glasses except by the two ends. This frame was supported in such a manner that the glasses were vertical, with a space of a foot or thereabouts intervening between them and a sheet of white card-board placed beneath. The glasses so situated were of course capable of holding solutions, and it is evident that the light transmitted through them to the eye of an observer standing above must come through the flat ends of the cylinders, which were of uniform size, and equally illuminated from the white sheet below. It is evident, too, that any alteration in the bulk of the liquid will not affect the quantity of light that enters by the end of the cylinder; and that the fact of all experiments being comparative will eliminate all errors that might have arisen from the difference of light at different hours, or any similar cause. As this little apparatus will be frequently referred to, I will give it a name, and since its principal use is in judging by the eye of the quantity of colour in two solutions, it may be appropriately designated the *Isoscope*.

For the purpose of determining whether the addition of water to a saturated solution of a salt causes it to absorb more or less light, the solution to be examined was divided equally between the two cylindrical glasses, so that when they were looked through from above they appeared identical in colour; water was then added to one of them, and if any change was effected by it, it became at once visible by comparison with the other. It was found neces-

sary to avoid focusing the eye at any particular part of a solution, when diluted so as to be very deep, but a little practice will soon enable the observer to avoid this, especially when the solutions are looked at from some considerable distance (five or six feet) above them. It is desirable also to place the head in such a position that the line joining the two eyes shall be at right angles to the line joining the two glasses, for if each eye be immediately over one of the glasses, a slight fallacy results, apparently from the unequal strength of the two eyes. The accuracy with which slight differences in intensity of colour may be observed, varies with the nature of the colour, the degree of illumination, and doubtless the sensitiveness of the observer's eye. In my case I can generally detect, under ordinary circumstances, a variation of 1 in 50. Differences in the *character* of the colour are, of course, easily recognized.

In this manner, the saturated solutions of many simple salts were examined, and where the saturated solution was too intensely coloured to be practically available, a slightly diluted solution was placed in each glass, and with one of them additional water was mixed. The following salts appeared to be unaffected by water, as to their power of absorbing the rays of light :—

Ferrous sulphate.	Terchloride of gold.
Ferric nitrate.	Terbromide of gold.
Ferric meconate.	Protochloride of platinum (in
Ferric comenate.	hydrochloric acid).
Ferric comenamate.	Bichloride of platinum.
Ferric gallate.	Bichloride of palladium.
Nitrate of nickel.	Chromate of potash.
Nitrate of cobalt.	Ferrocyanide of potassium.
Sulphate of copper.	Ferridcyanide of potassium.
Chloride of chromium.	Nitroprusside of sodium.
Acetate of chromium.	Sulphindigotic acid.
Chromate of chromium.	Sulphindigotate of ammonia.
Nitrate of uranium.	Carbazotate of copper.
Chloride of uranium.	Pentasulphide of potassium.
Sulphate of ceric oxide.	

Some dissolved salts were found to vary in the intensity of their colour, but not in the character of it, on dilution, thus :—

Ferric acetate became considerably darker.
Ferric tartrate became slightly paler.
Chromic sulphate (green) modification became paler.

Many dissolved salts were found to vary in the character of their colour, according to the state of dilution, thus :—

Ferric chloride becomes more yellow, that is to say, passes from a red orange to an orange yellow.

Ferric citrate becomes paler and more yellow.

Ferric sulphocyanide changes from an intense and pure red to orange, and on further dilution to yellow; but when this colour makes its appearance a decomposition manifests itself by the formation of a yellow precipitate.*

Chloride of nickel passes from a yellow to a blue green.

Iodide of nickel suffers a similar change, though when strong it does not transmit so much light as the chloride does.

Chloride of cobalt becomes paler and of a more decided pink.

Iodide of cobalt passes from a deep green to pink.

Acetate of cobalt becomes slightly paler, and assumes somewhat of a yellower tint.

Sulphocyanide of cobalt passes from a magnificent purple blue through every shade of purple till it becomes of the ordinary red or pink colour of cobalt salts in solution.

Chloride of copper passes from green to blue.

Bromide of copper suffers a similar change.

Acetate of copper becomes much paler, and passes from a greenish to a more pure blue.

Permanganate of potash becomes paler and of a redder purple.

Chromic acid passes from red to an orange brown, then to a purer orange, which becomes paler on further dilution.

That these changes of colour are due to the action of the water, and not to any merely physical cause, is proved by the fact that dilution with alcohol does not occasion them. Chloride of copper, for instance, dissolves in absolute alcohol of a bright green colour, and chloride or sulphocyanide of cobalt of a magnificent bluish purple, but when examined by the isoscope, these solutions are found to be unaffected by the additions of more absolute alcohol, either in respect to the intensity or the character of their colour. If water be added to the alcoholic solution, the change of colour ensues more or less perfectly according to the relative amount of the two liquids; and if alcohol be added to a somewhat dilute

* This decomposition has been investigated by Dr. Claus; see Annal. Chem. u. Pharm. July, 1856. He seems to be unaware that the sulphocyanide may be diluted till it appears of a yellowish orange, without any precipitate forming, even after many days.

aqueous solution of these salts, the primary colour is more or less restored. Ferric sulphocyanide, however, seems to form an exception. A very large quantity of absolute alcohol produces the same change in the colour of this substance that a much smaller quantity of water does, and on long standing, a little yellow substance separates. I do not believe that this depends on any water in the alcohol itself; for that employed by me was of specific gravity 790, and it is hard to conceive that any trace of water should leave the strongest alcohol to act upon a salt, and effect a change which usually requires its presence in overpowering quantity.

A glance at the list of salts which change colour on the addition of water will suffice to show that they consist of little else than acetates, and a peculiar group of "haloid" salts, namely, compounds of chlorine, bromine, iodine, and sulphocyanogen, with iron, and the allied metals, nickel, cobalt, and copper.

These changes of colour, though consistent with the idea of the water added to a saturated solution decomposing more of the original salt MR, and thus forming more MO,HR, are very far from proving that hypothesis. They may be attributed to the formation of a higher hydrate; and other hypotheses might easily be invented. It seemed, however, a matter of interest to try whether the change of colour produced by water in a solution of such a salt as acetate of copper was analogous to the change that takes place on the addition of another hydrogen compound, for instance, hydrochloric or sulphuric acid[*] Now, in both cases, a reduction of the colour ensues; and in the case of the acid, it takes place in a diminishing ratio, that is, each addition of acid has a smaller effect (as compared with its quantity) than the preceding. Does the action of water exhibit a similar ratio?

Experiments were performed to determine this. A portion of a saturated solution of acetate of copper was divided equally between the two vertical glasses of the isoscope. The one was kept as a standard; to the other a known amount of the same saturated solution was added, and as that of course increased the colour, water was added till it was brought down again to that of the standard. The ratio between the amount of water added and the amount of coloured salt which it could render invisible, so to speak, gave what was required. Two experiments were made with the same solution.

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[*] Phil. Trans. 1855, pp. 222, 223.

Orig. amount of Acetate of Copper Solution.	Amount of Acetate of Copper solution added.	Water required.		Reducing effect of each addition of Water.	
		Exp. I.	Exp. II.	Exp. I.	Exp. II.
Pts.	Pts.	Pts.	Pts.	Per cent.	Per cent.
100	8	60	..	13·3	
100	16	116	..	14·3	
100	24	180	..	12·5	
100	32	244	..	12·5	
100	40	..	330	..	12·1
100	48	352	405	14·8	10·7
100	56	..	535	..	6·1
100	64	596	615	6·5	10·
100	72	..	790	..	4·6
100	80	980	975	4·2	4·3
100	88	..	1180	..	3·9
100	96	1500	1440	3·1	3·1

Both these experiments indicate that the effect of additional quantities of water is in a decreasing ratio, at least, after the addition of four or five times its bulk of water to the saturated solution, about which point the two experiments show a certain irregularity and discrepancy. About this point, also, the change to a somewhat purer blue takes place.

On mixing water with a solution of ferric acetate, the colour is considerably deepened, but on standing awhile, the solution becomes nearly as pale as originally.

The following series of observations was obtained with ferric sulphocyanide :—

Orig. amount of Ferric Sulphocyanide Solution.	Amount of Sulphocyanide Solution added.	Water required.	Reducing effect of each addition of Water.
Pts.	Pts.	Pts.	Per 100 pts.
100	10	24	4·2
100	20	44	5·0
100	40	80	5·5
100	60	128	4·2
100	80	204	2·6
100	100	296	2·2
100	120	384	2·3
100	140	468	2·4
100	160	556	2·3
100	190	692	2·2

Within the range of these observations, which, as may be supposed, did not commence with a saturated solution, and which terminated long before the salt became yellow, there is evidently more than one change of ratio in the reducing effect of successive additions of water. The ratio at first increases, then rapidly decreases, and attains a kind of uniformity, which, however, seems to show another but very slight rise and fall.

The irregularity of these results rather militates against the idea of water acting on salts in the same way as a hydracid.

A still stronger argument against this hypothesis was found on a comparison of the rays absorbed by dilute and strong solutions of those salts that vary in the character of their colour according to the amount of water. It invariably happens that the dilute solutions, while they transmit every ray that was transmitted by a strong solution of the same salt, transmit also some that were absorbed by it. To take a particular instance, blue sulphocyanide of cobalt absorbs at once those rays of the prismatic spectrum which lie about the fixed line D; the red sulphocyanide transmits them perfectly: hence it may be concluded that after a certain dilution no more blue sulphocyanide is left, a conclusion at variance with the supposition that HO acting on CoCsy (blue salt) produces $CoO,HCsy$ (red salt) $+ HO + CoCsy$, the amount of the last substance diminishing as the water increases, but never entirely disappearing. The nature of the absorption indicates rather that the strong solution contains the compounds present in the dilute solution *plus* some other; and a close prismatic examination of the 'haloid' salts that change colour has furnished me with a remarkable confirmation of this view. It is founded on the fact deduced by *a priori* reasoning in my paper on the use of the prism,[*] and demonstrated in a more recent paper,[†] that "when two bodies combine, each of which exerts a different influence on the rays of the spectrum, the one constituent will absorb certain rays, and the other certain other rays, and the dissolved salt itself will transmit only those rays which are not absorbed by either, or in other words, only those which are transmitted by both." Now strong solutions of ferric chloride, chloride and bromide of copper, chloride and iodide of nickel and of cobalt, exhibit not only the absorption due to the respective metals, but another absorption which can be identified with that produced by the halogens themselves when simply dissolved in water; while, when these solutions are diluted, they cease to produce this second absorption, and give precisely the same prismatic image as any compound of the same base with a colourless acid. This is explained in detail with figures in the paper already referred to.[†] It is certainly a suggestive fact, and shows, I think, most clearly, that there is some difference of arrangement among the elements of the dissolved salt and the water, according to their proportional

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[*] Quart. Journ. Chem. Soc. April, 1857.   [†] Phil. Mag. Dec. 1857.

amount, and the degree of temperature; but what is that difference? The peculiar absorbent power exerted by bromine shows itself in the green solution of bromide of copper, but there is certainly no free bromine present, and it will hardly avail us to suppose that such a solution contains the true CuBr, and that the change of colour on dilution arises from the formation of a compound of oxide of copper with the colourless hydrobromic acid; for there would still remain the question—why should bromine affect the light when in combination with copper, while it does not do so when combined with hydrogen, or potassium, or indeed any other metal beyond this particular group and the congeners of gold? Besides anhydrous bromide of copper, which certainly has the greatest claim to be considered CuBr, is not green but black.

DOUBLE SALTS.

The action of water on double salts is a still more complicated problem, for beside all the questions that arise in respect to simple salts, there is the additional inquiry—whether water separates the two constituents of which the double salt is composed. This latter question, however, is more capable of decision than some previously discussed.

That a double salt is not always resolved into the two simple salts which we suppose constitute it, requires no elaborate proof. The iodide of platinum and potassium dissolves easily in water, though the iodide of platinum itself is insoluble; while, on the other hand, the potassio-chloride is sparingly soluble, though each of the chlorides supposed to be contained in it dissolves readily in water.

It is very conceivable, however, that in some cases a partial decomposition may take place; indeed some of Professor Graham's experiments seem to indicate this. He states,[*] that when alum, or bisulphate of potash, is diffused, one of the constituents passes out of the cell in greater quantity than the other. Now if these double salts are partially decomposed by the water, this is precisely what might be anticipated; and there is nothing else than water present to decompose them.

Should water exert such an action, it might be expected that the action would be increased by the addition of more water.

* Phil. Trans., 1850, p. 19.

There are cases in which water, when added in above a certain amount, does decompose a double salt. Thus colourless crystals of the iodide of mercury and potassium will dissolve in a little water, but the addition of a larger quantity causes the separation of the insoluble yellow iodide of mercury; and water added to a saturated aqueous solution of sulphocyanide of silver and potassium gives a curdy precipitate of sulphocyanide of silver.* In each case the more water is added the more complete the decomposition.

As double salts in a crystallized condition sometimes differ considerably in colour or shade from the simple salt of that base to which the colour is due, it was thought that if an increasing decomposition by water took place, it would make itself visible by a change of colour or shade when a strong solution was diluted in the isoscope. It was found, however, that the solution of a double salt containing a coloured constituent, has, generally speaking, precisely the colour and shade of that constituent; thus 200 grms., or one equivalent, of crystallized sulphate of copper and ammonia, gives precisely the same chromatic appearance when dissolved in water as 125 grms., or one equivalent, of crystallized sulphate of copper. Thus it was impossible to derive any information from the fact, that a solution of that salt, or the corresponding potash salt, or potash chrome alum, or the sulphate of nickel and potash, did not change in colour when diluted. The double chloride of platinum and potassium, the double iodide of the same, the analogous gold salt, and the hydrochlorate of chloride of gold, are also unaffected in colour by the further addition of water. What is more to the point is this—that the red bichromate of potash does not pale in colour on dilution, or become more yellow, as would be the case were more of the free acid and the neutral potash salt formed; and the bicomenamate of iron, which is red, remains unchanged, although the neutral salt is purple, and the comenamic acid itself colourless.

On the other hand, instances are not wanting of double salts, the solutions of which change colour on dilution. Thus, the compounds of chloride of copper with chloride of sodium, chloride of ammonium, chloride of platinum, or hydrochloric acid, though green when dissolved in the minimum of water, become blue on dilution, just as chloride of copper itself does; but they require a larger amount of water to produce the change than is requisite in the case of the simple salt. Red potassio-chromic oxalate varies

· * Described by Gössman, Ann. Pharm. Oct. 1856.

in intensity of colour by dilution, becoming sometimes paler, and at other times darker. The strong solution of white iron alum becomes redder on dilution, and Rose * has shown this to be due to the formation of a slightly soluble basic salt.

If a double salt be resolved on solution more or less into its simple salts, each of these will assuredly obey the law of reciprocal decomposition with any other salt that may be present. That this reciprocal action does take place between an ordinary and a double salt is beyond question; but that the elements of the latter have separated to produce it, is not so easily ascertained. One form of the experiment, however, occurred to me that seemed to be of a somewhat crucial character. Acetate of copper is of a much deeper blue than an equivalent amount of the sulphate, and this last, as stated above, is identical in colour with the double potash salt. If on mixing the sulphate of copper and potash with the acetate, the double salt should preserve its integrity, it is not very easy to conceive of a reciprocal decomposition, for the acetate itself is strictly monobasic, but if the double salt should separate to any extent, the free sulphate of potash will certainly suffer reciprocal decomposition with the acetate of copper, and as a portion of the copper will then be combined with sulphuric acid, a reduction of the colour will ensue. Accordingly, two equal portions of acetate of copper solution were mixed in the isoscope, the first with an equivalent of sulphate of copper, the second with an equivalent of double sulphate of copper and potash. The second mixture appeared somewhat lighter in shade than the first, and on the addition of three equivalents to each, the second became of a distinctly purer and paler blue. A similar experiment was made with the intensely scarlet bromide, and the pale yellow hydrochlorate of the chloride of gold. The addition of the latter compound reduced the colour of the bromide, though of course the mixture contained a larger amount of gold than the scarlet solution. It may be objected to this reaction that there probably exists a hydrobromate of the bromide of gold analogous to the chlorine compound; but that will not account for the reduction of colour, since the addition of hydrobromic acid to the neutral bromide does not render the solution paler.

In respect, then, to double salts it may be concluded that some are resolved by water more or less into two distinct salts, while

* Pogg. Ann. lxxxiii, 132.

others preserve their integrity in solution; but what determines this difference does not yet appear.

In respect to the general question of the chemical action of water on a soluble salt, I feel that no satisfactory conclusion has yet been arrived at; the idea that a reciprocal decomposition takes place between the two compounds has received no confirmation from my inquiry, unless in exceptional cases. The results rather militate in my opinion against that supposition, and tend to convince me more and more that the actual state of a dissolved salt is beyond the expression of any of our formulæ.
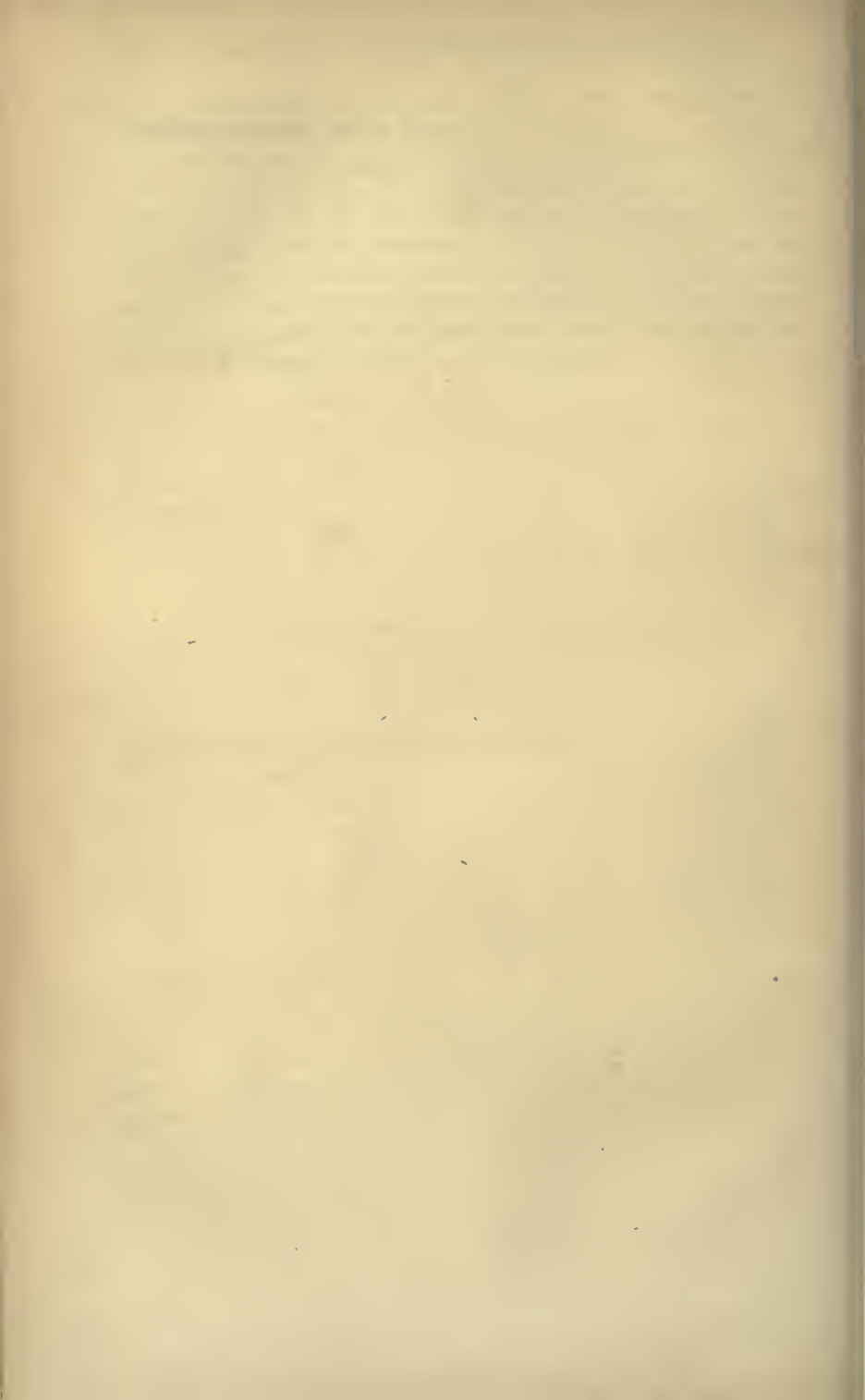
ON

COLLYRITE,

AND A NATIVE

CARBONATE OF ALUMINA AND LIME.

BY

J. H. GLADSTONE, Ph.D., F.R.S.,

AND

G. GLADSTONE, F.C.S.

A T Hove, near Brighton, is an old quarry in the upper chalk that presents some appearances of more than ordinary interest. Among these are the faults which have traversed the strata and broken the layers of flint, splitting them in every direction, and reducing them in some places almost to powder. Some of these fissures are filled up with a mineral whiter than the surrounding chalk, and perfectly distinct from it, which runs also along the dislocated layers of flint, and frequently imbeds the fragments.

This very white mineral occurs in rounded masses easily disintegrated in water. It is very soft, easily friable, with an earthy fracture, of low specific gravity, porous, and slightly hygroscopic. The external portions are frequently stained red with sesquioxide of iron. When examined chemically, it was found to consist mainly of hydrated silicate of alumina, perfectly decomposable by strong hydrochloric acid. There was also a varying amount of carbonic acid and of lime. The alumina was found to be free from phosphoric acid; nor was it mixed with glucina, a small quantity of which has been recently found so often to accompany this earth. The mineral, when strongly heated, gave off both the combined water and the carbonic acid.

For analysis the mineral was pounded and allowed to stand over sulphuric acid *in vacuo* till freed from all hygroscopic moisture. The determination of the different constituents was made in the usual manner.

A very soft, pure-looking specimen gave the following proportions :—

Silicic acid	14·49
Alumina	47·44
Carbonic acid	0·79
Lime	0·89
Water and loss . . .	36·39
	100·00

The carbonic acid and lime, being in very nearly equivalent proportions, may be assumed to have existed in combination ; and as they form together only 1·68 per cent., they may be considered as no constituent part of the aluminous mineral.

Excluding them, the results of analysis are as given below in the first column. The second column gives the theoretical proportions calculated from the formula $SiO^2, 2Al^2O^3 + 9HO$.

It is perfectly clear that the silicic acid and the alumina are in this ratio, but the amount of water is rather low for 9 equivalents.

	I.	II.
Silicic acid	14·74	14·14
Alumina	48·25	48·02
Water	37·01	37·84
	100·00	100·00

The mineral agrees, both in physical characters and in chemical composition, with that which has been described under the name of Collyrite, and to which the formula $SiO^2, 2Al^2O^3 + 10HO$ has been attributed; but our specimen appears to have been purer, and to have given more accurate numbers for the disilicate of alumina than those analysed by previous observers.

But no two portions analysed gave exactly the same composition. Some had a larger amount of carbonate of lime : thus a piece which was considerably harder, and broke with a conchoidal fracture, was found to contain between 5 and 6 per cent. of lime-salt. Some had a much smaller amount of silica : thus a piece which very easily fell to powder, and had the specific gravity of 1·99, gave about the following proportions :—

Silicic acid	3·4
Alumina . . . . . *.	60·5
Carbonate of lime . . .	0·6
Water and loss	35·5
	100·0

But the most remarkable specimens were from another part of the quarry. They had the same physical characters as those already described; but quantitative analysis showed that they contained more carbonic acid than was necessary to saturate the lime, and that there was no other base present except the alumina. Now as bicarbonate of lime is soluble in water, and carbonate of alumina is unknown as a mineral species, and has seldom, if ever, been procured even in the laboratory, it seemed desirable not to depend on one analysis. A quantity of one specimen was therefore pounded up and several determinations were made of each constituent, and that by different processes, the mean results of which are given in the first column of the subjoined Table. Another specimen was reduced to powder, and exposed over sulphuric acid *in vacuo* for a whole month, by which it lost no carbonic acid, but apparently a little of its combined water. It gave the analysis in the second column. Other specimens yielded the numbers in columns III. and IV.

	I.	II.	III.	IV.
Silicic acid . . .	6·22	5·87	5·41	5·30
Alumina . . .	41·04	39·58	36·32	40·51
Carbonic acid . .	10·91	14·77	18·15	14·14
Lime	7·37	11·22	11·62	9·18
Water . . .	33·16 ⎱	28·56	29·16	30·87
Traces and loss .	1·30 ⎰			
	100·00	100·00	100·66	100·00

Now in each of these cases the carbonic acid is far more than sufficient to neutralize the lime. Thus

7·37 parts lime neutralize	5·79	parts carb. acid, leaving	5·12
11·22 ,, ,, ,,	8·81	,, ,, ,, ,,	5·96
11·62 ,, ,, ,,	9·13	,, ,, ,, ,,	9·02
9·18 ,, ,, ,,	7·20	,, ,, ,, ,,	6·94

In what way is this excess of carbonic acid combined? It never exceeds in amount that which would be required to form bicarbonate, but in three instances it nearly approaches that quantity, hence the lime might be conceived as existing as such; or it might be carbonate of alumina; or a double carbonate of lime

and alumina; or collyrite in which part of the silicic acid is replaced by carbonic acid. But each of these suppositions has its difficulties. Bicarbonate of lime in a solid form is unknown; yet it is conceivable that alumina, by its remarkable power of withdrawing other substances from solution, might have enabled such a bicarbonate to exist in combination with itself. Of the existence of any carbonate of alumina we have as yet no proof, whether as a mineral or a production of the laboratory. A double carbonate of lime and alumina was purely hypothetical. The partial substitution of carbonic for silicic acid has not hitherto been recognized, that we are aware of, in mineralogical chemistry; and though the results of analysis of the first and second specimens given above would accord very well with that view, yet the third and fourth specimens show too much silicic acid, unless indeed we suppose that they were derived from a collyrite much richer in silica than those hitherto examined.

If in the above analyses we view the lime and carbonic acid as wholly in combination, and reject them as adventitious, the remaining mineral will have very nearly the same composition in the four specimens, and that composition will be that of the previous specimen, minus half its silica, or $SiO^2, 4\,Al^2\,O^3, 20\,HO$.

	I.	II.	III.	IV.	Theory.
Silicic acid	7·8	8·0	7·8	7·3	7·7
Alumina	51·0	53·0	51·1	52·4	51·5
Water	41·2	39·0	41·1	40·3	40·8
	100·0	100·0	100·0	100·0	100·0

In order, however, to solve if possible the question of the excess of carbonic acid, a portion of the fourth specimen was finely powdered, diffused through water, and exposed to a stream of carbonic acid; the gas dissolved out a little carbonate of lime, which was precipitated and found to amount to 0·8 per cent. It seemed incapable of dissolving out any more, leading therefore to the conclusion that the amount of carbonate of lime, existing as such in the mineral, is only a trace, and that the remainder is in some form of combination with the alumina. The powdered mineral, which had been acted on by a very large amount of the gas, was afterwards analysed, and found to contain very nearly all its original carbonic acid and lime.

Extending our inquiry we attempted to form an analogous compound artificially, and at once obtained a double carbonate of alumina and lime, in which the carbonic acid was to the lime in the ratio of three to one, and another where the ratio was similar to that in the mineral.

Another fact which bears on the state of combination of this excess of carbonic acid is the following :—If the mineral, after having been dried *in vacuo*, is exposed to a temperature of 100° C., it does not lose either water or carbonic acid; but if it be heated more strongly, though not even to incipient redness, it parts not only with the water and the excess of carbonic acid, but also with a portion of that required to neutralize the lime, and if to dull redness in a covered crucible, it parts with nearly the whole of its carbonic acid; yet a little remains which cannot be driven off, even if the temperature be greatly raised. Now it might be expected that simple carbonate of alumina or a carbonated collyrite would be decomposed at a low heat, or that bicarbonate of lime would be reduced to the common carbonate; but the easy expulsion of the remaining carbonic acid is not very compatible with either of these suppositions, and appears rather to point to a double carbonate which yields up all its carbonic acid more freely than carbonate of lime does. The small quantity of undecomposable carbonate of lime left may either have existed as such originally, or may have been formed during the decomposition of the double salt.

We are disposed, therefore, to regard this mineral as collyrite mixed with a varying amount of a hydrated double carbonate of alumina and lime. If it should bear a distinct name, it may be termed Hovite, from the place where it was first recognized.

On looking over published analyses of silicates, it did not appear that a carbonate had often been found entering into the composition of such minerals, yet there is a perfectly analogous instance on a smaller scale. Allophane is another hydrated silicate of alumina, and it occurs in a chalk-pit at Charlton, also in the upper chalk, and under circumstances almost identical with those under which we found the collyrite at Hove. In Mr. Dick's analysis of this[*], and in the analyses of four different specimens by Mr. Northcote[†], there was always found more carbonic acid than was required to saturate the lime. In none of these instances, however, did it exceed 1·31 per cent., and Mr. Northcote propounded no other view than that it existed as a bicarbonate.

On inquiring about the quarry at Charlton from which this mineral was obtained, we were informed by Mr. Church that the allophane was accompanied by a substance resembling our collyrite. Some of this was obtained, and the two following analyses were made of portions having rather different physical characters.

[*] See Professor Morris's paper, Quart. Journ. Geol. Soc. vol. xiii. p. 13.
[†] Phil. Mag. May 1857.

The first was more compact and more vitreous in its fracture than the specimens from Hove, and not so perfectly white. It more closely resembled the specimens of collyrite in the British Museum. On analysis it was found to be a silicate of alumina soluble in acids, with a little carbonate of lime. A portion which had been pounded and allowed to stand two days over sulphuric acid, lost 7·12 per cent. of water when heated to 100°C. The following was the analysis made :—

Silicic acid	16·58
Alumina	44·51
Water expelled above 100° C. and some Carbonic acid . .	34·17
Lime and loss	4·74
	100·00

This shows a somewhat larger proportion of silicic acid in comparison with alumina than any of the preceding analyses, and indicates that the mineral was intermediate between allophane and collyrite, in chemical composition as in physical properties. The carbonic acid did not appear to be in excess of the lime.

The second portion was very white and soft; after being dried *in vacuo* it did not give off water when heated at 100° C. It dissolved readily in hydrochloric acid with formation of gelatinous silica.

The results of analysis were as follows :—

Silicic acid	4·31
Alumina	59·08
Water	35·03
Carbonate of lime, and loss . . .	1·58
	100·00

This is almost identical with one of the specimens from Hove.

Altogether these hydrated silicates of alumina, many of which have been analysed and described under the names of allophane and collyrite, appear to form a series in which the silicic acid varies greatly in proportionate amount. They may be viewed as a hydrated silicate of definite composition, combined with indefinite amounts of the native hydrate of alumina, Al^2O^3, 3HO, Gibbsite. But what is this definite silicate? Collyrite, $2(Al^2O^3)SiO^2$, 9HO plus $6(Al^2O^3, 3HO)$, would give numbers almost identical with those of the last analysis recorded above; but collyrite itself might be viewed as allophane plus some equivalents of hydrate of alumina, and Mr. Northcote views

allophane as a still higher silicate combined with different proportions of the hydrate. All these formulæ might also be expressed as Dr. Odling's ortho-silicate, $Al^4 SiO^4$, plus more or less hydrate of alumina, plus more or less water; but not one of these methods of expression appears to possess any such preponderating advantage as to lead to the conviction that it represents the true composition of the mineral under its various phases.

ADDITIONAL NOTES

ON

RECIPROCAL DECOMPOSITION

AMONG

SALTS IN SOLUTION.

Additional Notes on Reciprocal Decomposition among Salts in Solution.

By J. H. GLADSTONE, Ph.D., F.R.S.

SINCE the publication of my paper on "Circumstances modifying the action of Chemical Affinity,"[*] and of "Some experiments illustrative of the reciprocal Decomposition of Salts,"[†] I have from time to time thought and experimented further upon the subject. The present communication is simply a gathering together of such observations as appear to me capable of throwing additional light on these laws of combination.

I reserve to some future occasion the experiments I have made on the time required to bring about a perfect state of equilibrium among various salts in solution, as the results are not yet sufficiently matured for publication, and the subject is a very distinct one.

The ultimate disposition of the various elements in solution is independent of the manner in which they were originally combined.

Suppose there be two basic elements M and M', and two salt-radicles R and R'; the question is, whether if MR' be added to

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[*] Phil. Trans., 1855, 179.   [†] Chem. Soc., Qu. J. ix, 144.

M'R in solution, the same distribution of elements will take place as if MR were added to M'R'. From the law of reciprocal decomposition it follows, as something like a corollary, that it must be so, and in my first paper I was content with one quantitative experiment; yet, as the opposite has been contended for, I thought it well to test the law in other instances.

The former experiment was this :—Two solutions were prepared, the one containing equivalent proportions of sulphocyanide of potassium, sulphate of potassium, and ferric nitrate; the other, equivalent proportions of sulphocyanide of potassium, nitrate of potassium, and ferric sulphate. These two mixtures, each containing the same absolute quantity of salts, were made up to the same volume with water; and the resulting colour was found to be identical, leading to the inference that the ultimate distribution of the four salts in each solution was the same.

The law was tested with a mixture of single equivalents of acetate of copper and nitrate of lead, and a mixture of single equivalents of acetate of lead and nitrate of copper. The colour was identical. A similar result was also obtained with sulphate of copper and nitrate of potassium, as compared with nitrate of copper and sulphate of potassium.

But it would rarely happen that a result perceptible to the eye could be obtained in this manner. The majority of metals that give colour to their compounds produce (unlike iron and copper) the same or nearly the same tint with whatever radicle they may be combined; and the same holds good with the colour-producing acids; whilst the great multitude of salts are colourless, and therefore invisible in solution. It occurred to me, however, that perceptible reactions might be obtained with these also, if mixtures were made of two colourless salts and then added to some coloured salt, such as ferric sulphocyanide, which is capable of reduction in colour by a redistribution of its components. The amount of alteration in this third salt would, of course, depend on the proportion of all the four salts ready to act upon it; indeed, the question would just be enlarged so as to include six elements instead of four —M, M', and M'' with R, R', and R''.

The experiment was tried in this manner :—Equivalent quantities of the sulphate and nitrate of potassium, and the sulphate and nitrate of magnesium, were dissolved in equal volumes of water; a mixture was made of equal quantities of the solutions of sulphate of potassium and nitrate of magnesium, and another mixture of equal

quantities of the solutions of sulphate of magnesium and nitrate of potassium : these were added to two equal portions of a solution of sulphocyanide of iron in the isoscope ; and the diminution of the colour effected by them was observed. Now, the sulphate of potassium is known to have a much greater power of reducing the sulphocyanide than the nitrate has, but it was found that the two mixtures produced exactly the same tint.

In like manner, acetate of potassium with nitrate of lead produced the same diminution of colour (within the limits of probable errors of experiment) as acetate of lead and nitrate of potassium. The same two mixtures were tried also on ferric meconate, and gave a similar result.

The same experiment on the red sulphocyanide was also made with mixtures respectively of sulphate of copper with nitrate of of magnesium, and sulphate of magnesium with nitrate of copper. The same shade was produced by each.

A similar result was obtained with chloride of sodium mixed with sulphate of magnesium, and sulphate of sodium mixed with chloride of magnesium. These two mixtures were also tried on the deep scarlet bromide of gold, and they were found to produce an equal reduction of the colour. The two had the same effect likewise on a solution of the double iodide of platinum and potassium.

Two solutions were prepared, the one of the double sulphate of copper and potassium, the other of an equivalent of sulphate of potassium mixed with an equivalent of sulphate of copper. They produced the same effect on a solution of ferric sulphocyanide. This experiment is of importance, not because there was much doubt, *à priori*, that the condition of a double salt in solution is the same whether it has ever been crystallized or not, but because at first sight some experiments recorded by Professor Graham seem to point to the opposite conclusion. He found, in respect to the salt above mentioned, and the sulphate of magnesium and potassium, that the double salt was more diffusible than its mixed constituents.* Yet this seems to be the case only when the solutions are freshly prepared and in the cold, and the discrepancy probably arises solely from the slowness of the action by which uniformity is ultimately produced.

When there are several salts with the possibility of solid matter forming, the ultimate result may indeed be influenced by the order

* Phil. Trans., 1850, 22.

in which they are mixed. Thus, in the experiment above narrated, with chloride of sodium and sulphate of magnesium compared with chloride of magnesium and sulphate of sodium, it was only when the salts were mixed together beforehand that they equally reduced the iodide of platinum and potassium. When they were added one after the other to the red salt, a deposit of platinum separated in the one case, though not in the other. This, however, is not a real exception to the general rule, which only refers to salts actually in solution.

Extension of M. Margueritte's experiment.

M. Margueritte has shown,* by a number of instances, that if a salt MR is less soluble in water than another salt M'R', or than MR' or M'R, the addition of M'R' causes a larger quantity of it to be dissolved. One instance is that of chlorate of potassium, which is more soluble in a solution of chloride of sodium than in pure water. Now, from the law of reciprocal decomposition (of which this is a result), it was foreseen that after a single equivalent of the more soluble salt M'R' had exerted its influence, a second equivalent would produce an additional effect, though to a smaller extent, and so on. On trying the experiment, this was found to be the case. 129 grm. of chlorate of potassium and 59 grm. of chloride of sodium were taken as equivalent proportions.

Chlorate of Potassium.	Chloride of Sodium.	Water required for solution.	Decrease for each equiv. of Chlor. Sodium.
1 equiv.	0	2493 meas.	0
1 ,,	1 equiv.	2208 ,,	285 meas.
1 ,,	2 ,,	2060 ,,	148 ,,
1 ,,	4 ,,	1910 ,,	75 ,,

If a compound MR *is rendered more soluble by the presence of another compound* M'R', *the addition of either* MR' *or* M'R *will precipitate it from its saturated solution.*

This is also a necessary consequence of the law of reciprocal decomposition: for the MR' or M'R will produce more MR, and the liquid is incapable of holding any more of this compound in solution. In a former paper, I examined one particular case

* Comptes rendus, xxxviii, 304.

of this general law, namely, when a salt insoluble in water dissolves in an aqueous solution of an acid; and the law was found to hold good in every instance except one. That apparent exception was in the case of ferric phosphate dissolved in hydrochloric acid, from which a precipitate was not obtained by the addition of phosphoric acid; but I have since found that phosphate of iron, freshly prepared by double decomposition, and well washed, dissolves in phosphoric acid, and thus the anomaly is fully explained. I have lately observed another apparent exception in the case of phosphate of calcium dissolved in hydrochloric acid, and this admits of another explanation, for the tribasic phosphate dissolves in three equivalents of the acid; therefore, if on the addition of phosphoric acid, any chloride of calcium be decomposed, the hydrochloric acid set free will suffice to dissolve the phosphate of calcium produced.

But in all these cases the compound MR was a salt scarcely soluble in water, and the more powerful solvent was an acid. Neither of these conditions is indispensable for the result. The following experiments will illustrate the general law in cases where 1st, the compound MR is soluble in water, though not so soluble as M'R', M'R, or MR'; 2nd, where M'R' is a neutral salt as well as MR.

1st—Sulphate of silver was dissolved in weak nitric acid; to a part of the solution nitrate of silver, and to another part sulphuric acid was added, with the production in each case of the crystalline sulphate.

Again, it was found that chloride of sodium had deposited from a solution of sulphate of sodium in hydrochloric acid; the liquid, which of course was saturated with the salt, and contained likewise free hydrochloric and sulphuric acids, and no doubt sulphate of sodium, was divided into two portions, and from each a crystallization of chloride of sodium was obtained by the addition, respectively, of sulphate of sodium and hydrochloric acid.

2nd—Where the solvent is a neutral salt. Chloride of lead was found to dissolve freely in acetate of sodium. Such a solution, saturated with the chloride, was prepared: it was divided into two parts; to the one neutral acetate of lead, and to the other chloride of sodium, was added, and in each case after awhile chloride of lead separated.

It appears, therefore, that the more general expression of the law deduced from theory, and given at the head of this section, is

confirmed by experiment. Yet it is not to be expected that in every case the precipitate will actually make its appearance; for the formation of a double salt or the special solvent powers of the compound added may be a disturbing influence, and may give rise to anomalous exceptions.

Action of Acid Solvents, and Reciprocal Decomposition in Alcohol instead of Water.

When ferric phosphate was dissolved in hydrochloric acid, the paleness of the solution, and the increase of colour on the addition of more acid, both rendered it evident to the eye that the whole of the iron was not in the state of chloride.   Indeed, a comparison of the colour gave ground for the belief that in a saturated solution, at least as much as 85 per cent. of the iron is actually held dissolved as phosphate in the acid present.* It became interesting to see whether this solvent action would take place in the absence of water; and if so, whether the same proportion between the different salts would be maintained.   For this purpose, a solution of hydrochloric acid in absolute alcohol was prepared, and its power of dissolving dry ferric phosphate was tried.   It dissolved a great deal, assuming a pale yellowish-green colour.   Thus, one question was answered; but there still remained the inquiry whether the proportions of the several salts in solution were the same as when the experiment was made in water.   This received a reply in the negative, showing that the nature of the liquid influenced the reciprocal action, for a comparison of the solution with one of ferric chloride in absolute alcohol showed that a very large quantity—probably 95 per cent.—of the iron must have been present as phosphate. Again, the alcoholic solution became much darker when diluted with water, which is not the case with the ferric chloride itself dissolved in alcohol.   Another experiment made with this solution of the phosphate was the following :—a portion was divided into two equal parts; to the one was added some of the hydrochloric acid dissolved in alcohol, to the other the same bulk of pure alcohol.   At first the two appeared of the same colour, but after awhile that containing the large excess of hydrochloric acid became decidedly deeper.†

* See Chem. Soc., Qu. J., ix, 152.

† Some of the experiments described in this and the preceding section were brought forward at the meeting of the British Association at Leeds, in 1858, but the subject has been more fully worked out since.

Testimony from Diffusion Experiments.

I have already published* an account of an experiment showing that, from a mixture of equivalent proportions of chloride of sodium and nitrate of barium there diffused the four substances in such relative proportions as could only be explained on the assumption that each of the two acids had distributed itself between the two bases.†
Professor G r a h a m, in his recent paper "On Liquid Diffusion applied to Analysis," has described two experiments of a similar character; the one made with a mixture of chloride of potassium and sulphate of sodium, the other with equivalent proportions of chloride of sodium and sulphate of potassium; but the results are not so conclusive in favour of the law of reciprocal decomposition, for the numbers do not differ widely from such as might be given if all the chlorine were in combination with the potassium, and all the sulphuric acid with the sodium. Yet the accordance is not perfect, and the distribution of the four elements may be very different. One thing is conclusively shown by the perfect accordance of the two experiments, namely, that, in the words of G r a h a m, "The acids and bases are indifferently combined, or that a mixture of chloride of potassium and sulphate of sodium is the same thing as a mixture of sulphate of potassium and chloride of sodium, when the mixtures are in a state of solution."‡

A Method of Quantitative Determination by means of Circular Polarization.

An argument in support of the law of reciprocal decomposition has already been drawn from an experiment made by B o u c h a r d a t,§ while examining the circular polarization of camphoric acid. He found that certain camphorates rotate the plane of polarization less than the acid itself, and that when one of these salts was supersaturated with hydrochloric acid, the solution did not exhibit so much polarizing power as it would have done had the whole camphoric acid been set free. Unfortunately, the experiment was not made with equivalent proportions of the different substances, and hence it has no quantitative value.

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* British Association Report, 1860, and Chem. News, Aug. 11th, 1860.

† The relative proportions in the diffusate expressed in equivalents were—sodium 1,253, chlorine 1,175, barium 812, nitric acid 892.

‡ Phil. Trans., 1861, 197.

§ Comptes rendus, xxviii, 319.

It occurred to me, however, that interesting numerical results might easily be obtained by taking advantage of the fact that different compounds of the same body rotate the plane of polarization differently; and just to test the possibility of this, I have made some determinations with two substances belonging to very different groups—nicotine and tartaric acid.

Nicotine gives a strong left-hand rotation, but when combined with hydrochloric acid it entirely loses this power.* A solution of known strength gave a rotation of $-14°$: it was mixed with an equivalent proportion of chloride of ammonium; the two odours of nicotine and ammonia were perceptible in the mixture, and when it was examined with the polariscope it indicated only $-10\cdot5$.

Hence it may be concluded, that sufficient nicotine to produce the wanting $-3\cdot5°$ of rotation had entered into combination with hydrochloric acid displacing of course an equivalent amount of ammonia. These numbers happen to have the common divisor $3\cdot5$. The four substances must therefore have been present together in solution in very nearly, if not exactly, the following proportions :

Nic HCl $+ 3$ NH$_4$Cl $+$ NH$_3 + 3$ Nic.   (Nic $=$ C$_{10}$H$_7$N.)
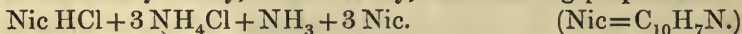
The experiment was repeated with chloride of sodium in place of chloride of ammonium. A rotation of $-28°$ was reduced to that of $-25°$ indicating the following composition for the mixture :

3 NicHCl $+ 25$ NaCl $+ 3$ NaO $+ 25$ Nic.

As the nicotine has decomposed less chloride of sodium than chloride of ammonium, and its absolute tendency to unite with the hydrochloric acid must have been the same in both experiments, it follows that the soda must have a greater tendency to combine with the hydrochloric acid than the ammonia has, as compared with their tendency to remain in combination with water alone. In combination with hydrochloric acid 3 equivalents of ammonia, in fact, balance themselves against the nicotine, and as many as 8·3 equivalents of soda are required to do the same.

It is evident that the above experiment might be repeated with innumerable other salts, and tables of respective affinity might thus be drawn up. The method is also available for experimenting on the influence of the quantity of any of the constituents.

Tartaric acid gave results which are not so easily understood. It has already been observed that equivalent proportions of the isomorphous tartrates of potassium and ammonium have an equal

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* Indeed, when the acid was in great excess, Wilhelmy's observation of a slight indication of right-handed polarization seemed to be confirmed.

influence on the polarized ray, and the same appears to be true of the sodium-salt. The amount of rotation is increased by the alkali, and apparently independently of whether it exists in the state of the neutral or acid-salt: thus :—

Tartaric acid   ..   .. $= +10°$
   ,, $+$ 1 equivalent of sodium (bitart.) $= +20·5$
   ,, $+$ 2 equivalents   ,,   (neut. tart.) $= +31·$

Tartaric acid was mixed with an amount of citrate of sodium, sufficient to form the bi-tartrate of sodium, if it should decompose it entirely. The polariscope showed that a partial decomposition had ensued. Additional portions of the citrate were added, and an additional production of the tartrate resulted in each case. The numbers were—

Tartaric acid   .   ..   . $= +10°$
   ,, $+ \frac{1}{2}$ citrate of sodium   .. $= +14·4$
   ,, $+$ 1   ,,   .. $= +18·5$
   ,, $+$ 2   ,,   .. $= +23·$

This result is in strict accordance with what was theoretically expected: the sodium has distributed itself between the two acids in certain proportions; namely, 8·5 to the tartaric, and 12·5 to the citrate, when equivalent proportions were employed; and when more citrate of sodium was added, more tartrate was produced.

Now, citric and tartaric are analogous acids, and perhaps the above is the true explanation of the phenomena observed; but when other salts of sodium were employed, results were obtained which showed some effect on the polarized ray that is not to be accounted for by such simple decompositions. Thus, with acetate of sodium—

Tartaric acid   ..   .. $= +10°$
   ,, $+$ 1 equivalent of acetate of soda $= +22°$
   ,, $+$ 2   ,,   ,, $= +28°$
   ,, $+$ 3   ,,   ,, $= +31°$

When two or three equivalents of the acetate were employed, the results obtained are intelligible enough, but why should a single equivalent of acetate of sodium produce a greater increase of rotation than a proportionate amount of hydrate of soda would have done?

But there are greater anomalies still. When nitrate sulphate

or chloride of sodium, or chloride of ammonium is added to tartaric acid it actually reduces the rotating power.   Thus :—

Tartaric acid	$= + 10°$
,, + 1 equiv. nitrate of sodium ..	$= + 7°$
,, + 2 equiv. ,, ,, ..	$= + 5°$
,, + 2 equiv. sulphate of sodium ..	$= + 8°·5$
,, + 2 equiv. chloride of sodium ..	$= + 3°·5$
,, + 2 equiv. chloride of ammonium	$= + 4°$

With sulphate of ammonia, a very slight increase of rotation was obtained.*

The cause of these phenomena has not yet been ascertained. It evidently will interfere with the use of tartaric acid for the purpose intended; but, doubtless other substances besides nicotine might be found to give trustworthy indications.

* Since the above was written, I have found that Biot has observed the remarkable changes in the rotation of the polarised ray by tartaric acid caused by dilution, or by combination with various other bodies. His experiments throw no light on the question of reciprocal decomposition.

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, March 13, 1863.

THE REV. JOHN BARLOW, M.A. F.R.S. Vice-President,
in the Chair.

JOHN HALL GLADSTONE, Esq. Ph.D. F.R.S.

On Fogs and Fog Signals.

DURING the course of the inquiry made by the Royal Commission on
Lights, Buoys, and Beacons, the attention of my colleagues and myself
was called to the fog signals which form part of the apparatus of
many lighthouses, and of all British light-ships. In the report we
expressed our conviction, "that they are not sufficiently powerful,
and recommend the provision of a more efficient warning in fog as
subject of investigation and experiment." About the same time,
some scientific men in Ireland stirred in the matter, and induced the
British Association to appoint a committee, at the head of which is
the Rev. Dr. Robinson, of Armagh, to bring the importance of the
subject more directly under the notice of the legislature. These
circumstances led me to turn my attention to fog; and I propose now
to lay before you some of the results arrived at, with reference both to
the meteorological phenomenon itself, and to the means adopted for
preventing its disastrous consequences among the vessels that sail along
our shores.

I have received voluminous returns of the occurrence of fog at
about 250 stations, for which I am indebted to the kindness of the
three general Lighthouse Boards,—the Trinity House, the Northern
Commissioners of Lighthouses, and the Ballast Board of Dublin; also
to the Board of Trade, through Admiral Fitz Roy; and to Mr.
Glaisher. I wish here also to express my thanks to several gentlemen
who have aided me in the preparation of this discourse, especially
Mr. Alexander Cuningham, who has just read a paper on the subject
at the Royal Scottish Society of Arts, and to our friend Professor
Wheatstone.

FOGS.

A fog is simply a cloud resting on the earth. In the first discourse
of the present season, Professor Tyndall explained the formation of

clouds from the aqueous vapour in the atmosphere; and defined a cumulus as "the visible capital of an invisible column of saturated air." A fog is the capital without the column. It is the moisture evaporating from the warm earth, or river, or sea, condensed at once by the colder air. Mr. Glaisher told us here how from his lofty position in the balloon, he saw a fog following all the windings of the Thames. This is a frequent observation, and it reminded me of a scene from the summit of the Righi one morning last summer. There lay in the valley of the Reuss a mist like a white sheet on the ground, but as the sun began to exert his power, and a light breeze to spring up, the uniform layer began to break into regular masses, and soon far beneath us there stretched a cirrus cloud, identical in aspect with those we so often see in the highest regions of the atmosphere.

Fog, then, is composed of minute particles of water, most likely in a globular form, for there seems to be no ground for the popular notion of vesicles of vapour. Smoke enters largely into the composition of that peculiar yellow fog which visits London a few times each year,—a fog of wonderful darkness and quietness, and strangely bewildering.

This condensed vapour has a great effect in obstructing the passage of light; the sun himself cannot look through it. A slight mist seems to attack principally the more refrangible rays of the spectrum, so that the light appears redder than usual. I once analysed with a spectroscope the rays which reached Worthing from the great revolving light on Beachy Head, twenty-eight miles distant, and found that those only situated between Fraunhofer's lines C and F were transmitted. This was on what would be called a clear summer night. An objection has been raised against the orange-red glass used in many of the French lighthouses, that in misty weather all bright lights are reduced to very nearly that colour, and thus the distinction is lost; a misfortune that could hardly happen with the deep-red glass employed for the red lights of the British Isles. When the sun shines through a cloud or mist, we do not detect those atmospheric lines which make their appearance when his disk is near the horizon. Yet I have observed in London, when the sun at a considerable altitude loomed red through a slight fog, that the characteristic C 6, δ, and η were visible.

There is, of course, every conceivable gradation between the lightest haze and the densest fog, and it is a difficult matter to draw a line of distinction between fog and mist. The value of the meteorological returns in my possession depends greatly on this, and there is reason to fear, even from internal evidence, that one lighthouse keeper calls by the name of fog what another keeper thinks sufficiently described as mist or haze. Yet these keepers have a certain general sentiment and similarity in their way of thinking, and with many the practical definition of a fog is when it is necessary to sound the signal. Among amateur observers on land the greatest discrepancy prevails; but nautical men seem to have a general agreement as to what amount of thickness is to give a claim to the designation fog. For such obser-

vations Mr. Cuningham suggests that a pole, painted vermilion, should be set up at a hundred yards from the station, and that such an amount of mistiness as renders it invisible should alone be named fog. The colour of the pole should, of course, be in strong contrast to the objects behind it. This definition is somewhere about that practically adopted by seamen; it has been accepted by Mr. Glaisher, and it is to be hoped that it will be generally adopted by all observers.

From the returns received, the following deductions may be drawn : —

I. While many fogs are quite partial in their character, others cover a large extent of country. The irregular distribution of a London fog is a matter of frequent observation. Thus, last Tuesday, the day of the royal wedding, one of the densest yellow fogs obscured Westminster, whilst at Bayswater there was nothing more than a murky mist. The long-continued fog of November last in London, extending from the 19th to the 25th, was observed also at Berkhampstead, Oxford, and Banbury, but other parts of England seem to have been clear. The occurrence of fog at the lighthouse stations all round the coast during the first six months of the year 1861 has been especially studied, and the fogs of that April have been represented on a map. Some of them cover large portions of the British Isles. For instance, that of the 14th stretched all round Ireland, except the south-west corner, crossed the Irish sea to the headlands of Wales and the south-western isles and coasts of Scotland, and made its appearance again across the mainland in the Firth of Forth.

II. Some months are marked by fogs much more than others. For instance, along the south coast of England, February and September are comparatively free, while January and June are foggy months. November is notorious for fog in London, but does not seem to deserve that character elsewhere.

III. Some years are much more visited by fogs than others. For instance, 1861 was freer than 1858 along most parts of the coast.

IV. Different localities are very variously visited by fog. England does not deserve that pre-eminent character for mistiness which is attributed to it by the popular imagination of the Continent. The value of the returns in showing the relative distribution of fog in different places is seriously affected by the different standards in the minds of the observers, but the following points seem pretty clearly made out : A fog is more uniformly distributed over the surface of the sea than on the adjoining coasts. Fog is not particularly prevalent about sandbanks, or low headlands; but where cliffs or high hills catch the south-west wind just after it has swept the ocean, as at the Isle of Wight, the Start Point, Lundy Island, and the Rocks of Pembrokeshire, the numbers run very high. The highest return is from Barra Head, the southernmost point of the Hebrides, where winds surcharged with moisture from the Gulf Stream strike the cold northern rocks, and wrap them in cloud or fog.

Fog Signals.

As light only very imperfectly penetrates a fog, attempts have been made to warn vessels of their approach to danger, or to acquaint them with their position, by means of sound. The fog signals actually in use are as follows :—Bells are employed at many of the lighthouses, and in the Irish light-ships, the finest, perhaps, being two near Dublin, and that at the Copeland Island, in the Irish sea, which is rung by machinery, and is said to have been heard thirteen miles off. At the end of the pier at Boulogne there is a large bell, in the centre of a large parabolic reflector facing the sea. It is struck by three hammers alternately, the motive power being a falling weight. Gongs are made use of in all the light-vessels belonging to the Trinity House. Guns are fired on board the Kish light-ship, from the mountain above the South Stack Lighthouse, at Fleetwood, and elsewhere. A very powerful steam-whistle has for some time been in operation at Partridge Island, near St. John's, New Brunswick, a part of the world peculiarly affected by fog.

At the Skerries, near Holyhead, terns and other sea-birds are encouraged, as their cries serve as a warning to vessels during fog ; but unfortunately some rats escaped from the 'Regulus,' which was wrecked there about seven years ago, and they are destroying the birds. A cat has been tried, but she preferred birds to rats.

The comparative efficiency of these various methods is a very serious question ; indeed, there are grave objections to the use of sound at all as a fog signal. The difficulties are as follows :—A sound indicates the proximity, but not the exact direction, of a danger. In this respect it is totally different from a light. Yet the mere warning is something ; and probably a suitable ear-trumpet would give a better idea of the direction than is obtained without it. There is evidence that vessels have sometimes steered by a sound ; for instance,—" In the winter of 1860, the steamer 'Iron Duke' having been drawn by the flood tide to the northward past Howth, was attracted by the sound of the bell, and steered by it safely towards Kingston, until the bell on the east pier of that harbour told her of its proximity, and ultimately led her into safety." The Royal Commissioners on Lights made special inquiry about the Boulogne bell, and found that some of the captains of steamers frequenting that port could find their way in by the sound of the bell, in thick weather ; at least, in conjunction with the use of the lead.

An objection to the use of most of these fog signals is the fear that they may be mistaken for other sounds, or other sounds mistaken for them. Bells are frequently being rung on shipboard ; the firing of guns is the well-known sign of distress ; and steamers in a fog are in the habit of whistling as they go along. Gongs do not seem open to this objection ; and in the case of other sounds, it might be obviated by having a definite system of repetition, as is done with the flashing

and revolving lights.   My friend, the Rev. T. Pelham Dale,* has indeed suggested a means of signalling, in which musical notes are employed.

Another difficulty is, that even loud sounds cannot be heard far to windward if a breeze is blowing; but this is of less importance, as a fog usually occurs in calm weather.

But the great objection to sound as a fog signal is, that a fog stops the waves of sound as it does those of light.   It is well known that sound will not traverse a heterogeneous medium, such as air loaded with mist.   As to the fact of such signals being rendered inefficient by the very thing which they are intended to penetrate, the testimony of mariners is somewhat conflicting.   Mr. Alexander Cuningham, who is the secretary of the Northern Commissioners of Lighthouses, says:—— "Many years ago, having landed from the lighthouse tender on the small skerry in the Portland Firth, a fog came on.   We hurried off in the hope of reaching the vessel; but before doing so, the fog shut her completely from our view.   We pulled in the direction (having a compass) in which the tender was last seen; but those who know the rapidity and variety of the tides in that dangerous locality, will easily be prepared to hear that our efforts were unsuccessful.   We lay about the spot for some time, firing our fowling-pieces, and at last pulled for the shore.   Next morning the vessel came in sight; and on comparing notes, we found that we must have been within a very short distance of her; and they had been firing small six-pound carronades all night, and we never heard them, nor did those on board hear our guns."

Yet, on the other hand, we have accounts of bells being heard at a distance of some miles during a fog, and the steam-whistle near St. John's is said by the captains and pilots of steamers frequenting that port to be most serviceable, and to be generally heard for four or six miles during strong breezes blowing on shore.   It is, indeed, quite possible that fogs of the same intensity may still have a very different effect upon the same signal, and that for two reasons; first, one fog may reach far up into the atmosphere, presenting a high wall to every vibration; while another may be a thick layer lying on the surface of the earth, with an open space above, through which the swelling waves of sound may freely pass.   Secondly, air perfectly saturated with moisture is no bad conductor of sound; a fog under such atmospheric conditions may therefore be far less obstructive than when the medium is more heterogeneous.

Considering these objections to the use of sound as a fog signal, must we abandon it altogether?   We cannot do so, as we have nothing better to substitute.   We fall back upon the recommendation of the Royal Commission, that further experiments should be made, which it is hoped will be gradually adopted by the authorities, as the majority of the other scientific recommendations have been.

Experiments should be performed on the manner and degree in which fog absorbs or destroys sounds of different pitch, or of different

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* Marryatt's Signals, ed. 1856.

characters,—for instance, a sharp sound or a prolonged sound ; on the various means of producing loud sounds, as to their pitch, volume, convenience, costliness, &c. ; whether a repetition of the same sound, or some variation in note, octave, frequency, &c., be desirable ; on the influence exerted by the height above the sea at which the sound originates ; on the influence of a background, such as a tower, cliff, or hill, in reflecting the sound, or of a concave mirror ; on the best means of directing a sound to a particular azimuth, or of determining its direction when on board ship.

Captains Close and Nisbet, of the Trinity Board, have made some experiments on one of these points at Holyhead Mountain, where a gun was fired from near the surface of the sea, and another at a considerable height, and the respective reports were listened to from various distances at sea. They found the upper gun was heard best for six miles, after which it lost its superiority. But the most remarkable result was the irregularity of the noise from the lower gun, which, at certain points in fact was not heard at all, though the flash was distinctly seen.

Powerful means of producing sound, besides those already mentioned, have been suggested. Mr. Cowper has planned a large steam-trumpet for lighthouse stations, which may be made to revolve. There is something similar in America worked by Erichsen's engine, with which is associated the name of Mr. Daboll. And Professor Holmes, of the Magneto-Electric Light, has also a steam-trumpet, which can be adapted for different notes, and gives a buzzing sound of wonderful intensity. Suggestions on this point were also made to the Royal Commissioners by several scientific men. Thus, horns were strongly recommended by more than one; but Mr. Mallet prefers explosive sounds ; and Sir John Herschel says :—" It would be worth trial, what would be the effect of a battery of whistles, blown by high-pressure steam, or by a combination of three, or several sets of three, pitched exactly to harmonic intervals (key-note, third, fifth, and octave), but all of a very high pitch, and with a rattle (analogous to the pea in a common whistle), which intensifies the action on the auditory nerve." Captain Ryder believes a gun might be constructed to produce the very distinctive sound of an explosion, followed instantaneously by a whistle.

There is another and very promising field for experiment, the transmission of sound through the water itself. The experiments of M. Colladon on the Lake of Geneva proved the great distance to which sound is transmitted through water, and the velocity and directness of its course.*

In his observations he employed a bell, let down into the water ; but this is a bad instrument for signalling, as its vibrations are almost instantly stopped. Many arrangements would appear to be preferable. The Syren, which was so called by its inventor, M. Cagniard de la

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* Mémoires de l'Académie des Sciences: Des Savans Etrangers.—Tome v.

Tour, because it would sing under water, is well adapted to give any note that is found desirable.* Long glass tubes, vibrating longitudinally, are said to produce immense volumes of sound in water: and other means might be devised. As the sound remains in the water, it would be necessary to make some communication between it and the ear of the listener. M. Colladon employed an apparatus like a spoon, with a tube for handle. By this means a mariner might listen for signals made at any important station, such as the Lizard Point, and might not only hear them at a great distance, but determine approximately their direction, unaffected by the state of the atmosphere above.

[J. H. G.]

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* Ann. Chim. Phys. xii., page 171.
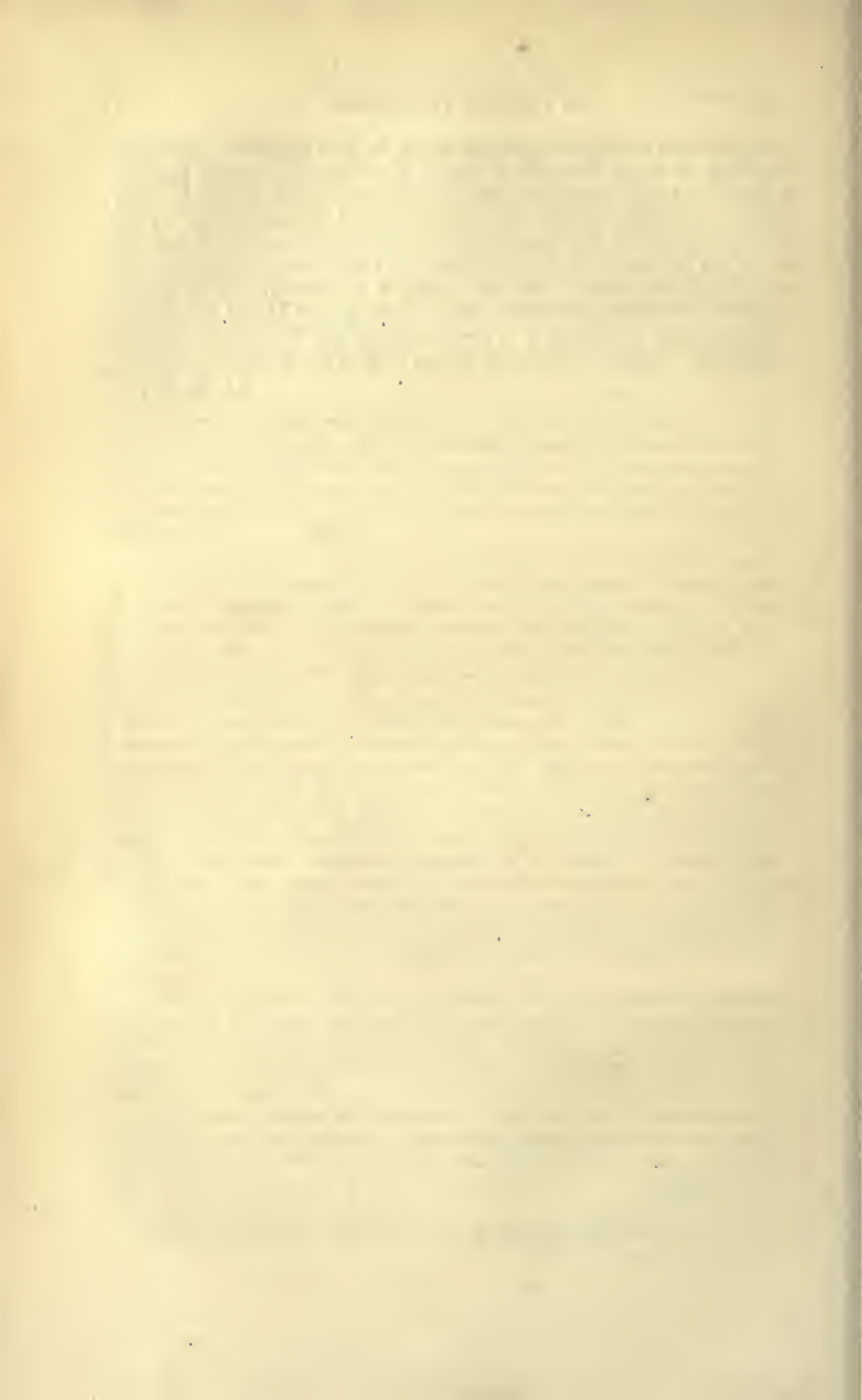
ON ESSENTIAL OILS.

Part I.

By J. H. Gladstone, Ph.D., F.R.S.

During the course of the inquiry into the refraction, dispersion, and sensitiveness of liquids, which was recently undertaken by me in conjunction with the Rev. T. P. Dale, several of the hydro-carbons isomeric with oil of turpentine were prepared and examined.* I have since then pursued the investigation much further, both in regard to the physical and chemical properties of different essential oils.

The frequent adulteration of these oils, as they are met with in commerce, renders it necessary to explain particularly how I came by the different specimens examined. Mr. S. Piesse, who took a scientific interest in the inquiry, supplied me, at cost price, with such samples as he believed to be quite genuine, either because he distilled them himself, or because he had full confidence in the manufacturers from whom he imported them. In this way I obtained specimens of the essential oils of bay, birch-bark, bergamot, cajeput, calamus, caraway, cascarilla, cassia, cedar, cedrat, citronella, cloves, dill, elder, Indian geranium, lavender, lemon-grass, mint, myrrh, neroli, nutmeg, orange, parsley, patchouli, peppermint, petit grain, rose, rosewood, santal-wood, thyme, verbena, wintergreen, wormwood, and a collection from the establishment of Mr. Scott, of Penang, of the oils of citronella, lemon-grass, nutmeg, and patchouli, which, being

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* See Phil. Trans., 1863, pp. 332, 340—342.

duplicates from another source, served to test at once the purity of each specimen, and the uniformity of the composition of the oil from different parts of the world.

I procured at the famous Spezieria of Santa Maria Novella at Florence, samples of the oils of anise, bergamot, lemon, myrtle, orange, and rosemary, all, I believe, distilled on the premises. I purchased also the small samples exhibited last year by Gillmeister, Cropp, and Co., of Hamburg, at the International Exhibition, namely, oils of calamus, caraway 1st distillation, and 2nd distillation, coriander, cubebs, and wormwood. Mr. J. W. Osborne, of Victoria, kindly furnished me with specimens of five of those oils which that colony displayed at the Exhibition. They were from *Atherosperma moschatum, Eucalyptus amygdalina, E. oleosa, Melaleuca ericifolia,* and *M. linarifolia.* I am also indebted to Dr. Stenhouse for allowing me to examine his specimen of laurel turpentine from a species of Ocotia from Demerara; to Mr. A. H. Church for some purified hydrocarbon from anise; and to the Chemical Society for the use of some solid essence of peppermint.

Within the last few days, Dr. J. H. Gilbert has kindly intrusted me with his specimens of two blue oils, the one from the wild chamomile (*Matricaria Chamomilla*) and the other from millefoil (*Achillea millefolium*); and Mr. E. Atkinson has given me a highly coloured specimen of patchouli from the south of France. I also wish to acknowledge the services rendered by my assistant, Mr. J. D. Holmes, especially in the chemical part of this inquiry.

My examination of these oils gave me no reason to doubt the genuineness of any of the specimens, the only sign of impurity being a little alcohol in one or two of those from Hamburg.

Crude Oils.

In the following table are given some of the physical properties of the crude oils: their specific gravity at 15° 5 C. (60° F.), the refractive indices of the lines A, D, and H, (or G, where the yellowness of the liquid prevented H being seen), and their power of rotating the plane of polarization. This last property is given for a tube of the length of 10 inches. Where a shorter tube for any reason was employed, the necessary calculation has been made. Thus, oil of dill was really observed in a tube of 5 inches, when it gave

103° of right-hand rotation, but it is put down as + 206°. The same length of a solution consisting of equal weights of cane-sugar and water, gives a rotation of 105°. The temperature was noted in all the later observations of this nature, but it is not recorded, as it would necessitate another column, and it appears that the difference of a few degrees makes little perceptible change in the rotating power of such of the essential oils as have been tested for this purpose.

Crude Oils.	Spec. Grav. at 15°·5 C.	Refractive Indices.				Rotation.
		Temp.	A.	D.	H.	
Anise	·9852	16°·5	1·5433	1·5566	1·6118	− 1°
Atherosperma Moschatum..	1·0425	14°	1·5172	1·5274	1·5628	+ 7°
Bay	·8808	18°·5	1·4944	1·5022	1·5420	− 6°
Bergamot	·8825	22°	1·4559	1·4625	1·4779G.	+ 23°
„ Florence	·8804	26°·5	1·4547	1·4614	1·4760G.	+ 40°
Birch-bark	·9005	8°	1·4851	1·4921	1·5172	+ 38°
Cajeput	·9203	25°·5	1·4561	1·4611	1·4778	0°
Calamus	·9388	10°	1·4965	1·5031	1·5204G.	+ 43°·5
„ Hamburg........	·9410	11°	1·4843	1·4911	1·5144	+ 42°?
Caraway	·8845	19°	1·4601	1·4671	1·4886	+ 63°
„ Hamburg, 1st dist.	·9121	10°	1·4829	1·4903	1·5142	..
„ „ 2nd	·8832	10°·5	....	1·4784	....	..
Cascarilla	·8956	10°	1·4844	1·4918	1·5158	+ 26°
Cassia	1·0297	19°·5	1·5602	1·5748	1·6243G.	0°
Cedar	·9622	23°	1·4978	1·5035	1·5238	+ 3°
Cedrat.................	·8584	18°	1·4671	1·4731	1·4952	+ 156°
Citronella	·8908	21°	1·4599	1·4659	1·4866	− 4°
„ Penang	·8847	15°·5	1·4604	1·4665	1·4875	− 1°
Cloves..................	1·0475	17°	1·5213	1·5312	1·5666	− 4°
Coriander	·8775	10°	1·4592	1·4652	1·4805G.	+ 21°?
Cubebs	·9414	10°	1·4953	1·5011	1·5160G.	..
Dill	·8922	11°·5	1·4764	1·4834	1·5072	+ 206°
Elder	·8584	8°·5	1·4686	1·4749	1·4965	+ 14°·5
Eucalyptus amygdalina....	·8812	13°·5	1·4717	1·4788	1·5021	− 136°
„ oleosa	·9322	13°·5	1·4661	1·4718	1·4909	+ 4°
Indian geranium	·9043	21°·5	1·4653	1·4714	1·4868G.	− 4°
Lavender	·8903	20°	1·4586	1·4648	1·4862	− 20°
Lemon..................	·8498	16°·5	1·4667	1·4727	1·4946	+ 164°
Lemon-grass	·8932	24°	....	1·4705	....	− 3°?
„ Penang.......	·8766	13°·5	1·4756	1·4837	1·5042	0°
Melaleuca ericifolia	·9030	9°	1·4655	1·4712	1·4901	+ 26°
„ linarifolia	·9016	9°	1·4710	1·4772	1·4971	+ 11°
Mint	·9342	19°	1·4767	1·4840	1·5015G.	− 116°
„	·9105	14°.5	1·4756	1·4822	1·5037	− 13°
Myrtle	·8911	14°	1·4623	1·4680	1·4879	+ 21°
Myrrh..................	1·0189	7°·5	1·5196	1·5278	1·5472G.	− 136°
Neroli	·8789	18°	1·4614	1·4676	1·4835G.	+ 15°
„	·8743	10°	1·4673	1·4741	1·4831F.	+ 28°
Nutmeg	·8826	24°	1·4644	1·4709	1·4934	+ 44°
„ Penang	·9069	16°	1·4749	1·4818	1·5053	+ 9

Crude Oils.	Spec. Grav. at 15°·5 C.	Refractive Indices.				Rotation.
		Temp.	A.	D.	H.	
Orange-peel...............	·8509	20°	1·4633	1·4699	1·4916	+ 32°?
,, Florence......	·8864	20°	1·4707	1·4774	1·4980	+ 216°
Parsley	·9926	8°·5	1·5068	1·5162	1·5417G.	− 9°
Patchouli	·9554	21°	1·4990	1·5050	1·5194G.	..
,, Penang........	·9592	21°	1·4980	1·5040	1·5183G.	− 120°
,, French	1·0119	14°	1·5074	1·5132	1·5202F.	..
Peppermint	·9028	14°·5	1·4612	1·4670	1·4854	− 72°
,, Florence......	·9116	14°	1·4628	1·4682	1·4867	− 44°
Petit grain	·8765	21°	1·4536	1·4600	1·4808	+ 26°
Rose	·8912	25°	1·4567	1·4627	1·4835	− 7°
Rosemary	·9080	16°·5	1·4632	1·4688	1·4867	+ 17°
Rosewood	·9064	17°	1·4843	1·4903	1·5113	− 16°
Santalwood..............	·9750	24°	1·4959	1·5021	1·5227	− 50°
Thyme..................	·8843	19°	1·4695	1·4754	1 4909G.	..
Turpentine..............	·8727	13°	1·4672	1·4732	1·4938	− 79°
Verbena	·8812	20°	1·4791	1·4870	1·5059G.	− 6°
Wintergreen	1·1423	15°	1·5163	1·5278	1·5737	+ 3°
Wormwood	·9122	18°	1·4631	1·4688	1·4756F.	..

From this table it will be seen that the specific gravity of these crude essential oils does not vary much, the large majority being about 0·9. The refractive index also of the large majority lies for A between 1·46 and 1·5, while the length of the spectrum, that is, the difference between the refractive indices of H and A, or $\mu_H - \mu_A$, is generally about 0·028. But the oils of parsley, atherosperma, myrrh, wintergreen, cloves, anise, and cassia, stand out as more refractive and dispersive, and, at the same time, specifically heavier. The oil of cajeput has less influence on the rays of light than any of the others.

The column of circular polarization, on the contrary, reveals the widest differences between these essential oils, both in the degree and in the direction of the rotation; but I fear no great reliance can be placed on this characteristic for distinguishing the oils; for it has been found that the rotation of different samples of the same oil varies widely, not only in the crude state, but even when the pure hydrocarbons themselves have been examined.

Nevertheless, it is possible that some of these physical characters may be of service in detecting the fraudulent admixture of oils. Thus the addition of oil of turpentine would, in almost every instance, have the effect of lowering the specific gravity, and contracting the spectrum. Again, pure oil of bergamot has a low

refraction, lower, doubtless, than those mixtures which are often sold under its name. The refractive index of D has been purposely included in the above Table, as that line can be always obtained either from daylight, or more conveniently still, from a soda flame. Any instrument maker could easily contrive a simple apparatus for testing in this way the refraction of samples of essential oils.

These crude oils were submitted to fractional distillation with the view of separating their different constituents. The hydrocarbons thus rectified were further purified by repeated distillation from sodium. The alkali-metal generally combines with the oxidized oils to form a resinous non-volatile substance; but it is impossible to say that it never produces from it a new hydrocarbon. A few of these compounds containing oxygen, for instance those of the different species of Melaleuca, may be distilled unchanged from sodium.

The following is a brief account of each of these oils :

Anise.—This essential oil is derived from the seeds of the *Pimpinella anisum.** It has been carefully examined by Messrs. Cahours, Laurent, and Gerhardt, and is known to consist principally of an oil containing oxygen, of the composition $C_{20}H_{12}O_2$, which has received the name *anethol*. It contains, also, a small quantity of a hydrocarbon closely resembling turpentine, which may be separated from anethol by rectifying the first portions of the distillate from sodium.

Atherosperma moschatum.—This is distilled from the dried bark of a tree which bears the above botanical name, and is also called the *Victorian Sassafras*. The specimen was of a pale yellow colour, and of a very peculiar odour. When distilled it began to boil at about 221° C. and passed over almost entirely at 224°C. This distillate is an oxidized oil of specific gravity 1·0386 at 20°C.

Bay.—This oil, from the berries of the *Laurus nobilis*, has the characteristic odour of the plant, analogous to that of cloves. The specimen examined had a brownish-yellow colour. When distilled it yielded, first, a hydrocarbon, which, when rectified repeatedly from sodium boiled at 171°C., and had a specific gravity of 0·8502 at 20°C. Two combustions were made with oxide of copper.

I. 0·3096 grm. gave 0·9975 grm. of carbonic acid, and 0·3345 grm. of water.

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* The names of the plants from which the essential oils are obtained are taken principally from Mr. Piesse's book, "The Art of Perfumery."

II. 0·3065 grm. gave 0·9867 grm. of carbonic acid, and 0·3374 grm. of water.

These analyses agree closely together, and are sufficiently near to the formula $C_{20}H_{16}$ to show that at least the great bulk of the rectified oil was of that composition. The following are the percentage proportions:—

	I.	II.	Calculated.
Carbon......	87·87	87·79	88·23
Hydrogen ..	12·00	12·23	11·77
	99·87	100·02	100·00

When this hydrocarbon had distilled over, the boiling point rose to 252°C., and another oil passed into the receiver. It dissolved readily in an aqueous solution of potash, from which it was thrown down by hydrochloric acid. This afforded the means of separating it perfectly from the hydrocarbon. It then had the properties of *eugenic acid*. It had the characteristic odour of that substance when fresh, and also, like it, became brown on keeping, with a peculiar alteration in the smell. Its specific gravity was 1·066 at 20°C. Its refractive index was 1·5402 for the line D, and 1·5539 for F at 18°C.: the indices for eugenic acid at the same temperature having been determined by Mr. Dale and myself at 1·5394 for D, and 1·5528 for F. To supplement the proof from these physical properties, the barium-salt was prepared, and the amount of base determined. When boiled with baryta-water, the oily body gave a solution which deposited white crystalline scales, becoming brown on exposure to air.

I. 0·287 grm. ignited in a crucible gave 0·120 grm. of carbonate of barium.

II. 0·385 grm. ignited in a crucible gave 0·165 grm. of carbonate of barium.

These yield the following percentages of barium, agreeing sufficiently well with that deduced from the formula $C_{20}H_{11}BaO_4$, eugenate of barium:—

	I.	II.	Calculated.
Barium	29·06	29·89	29·58

Bergamot.—The well-known oil obtained from the cells of the rind of *Citrus Bergamia*. Each of the specimens examined had

a pale green colour. It begins to boil at about 182°C. The first portions contain a little water and acetic acid, and a hydrocarbon resembling oil of lemon. At a higher temperature liquid hydrates of the oil distil over, and a small quantity of solid matter is left in the retort.

Birch-bark.—This oil is produced by the dry distillation of the bark of *Betula alba*. It gives its characteristic odour to Russia leather, which is tanned with this bark. When distilled, a considerable portion came over between 171°—193°C., which, when rectified several times from sodium, boiled at 170°—171°C., and had a specific gravity of 86·26, a refractive index of 1·4681 for A at 20° C., and a dispersion of ·0291. This, in conjunction with its odour of coal-tar, led to the idea that it consisted more or less of *cymol*. To separate any essential oil of the ordinary type, hydrochloric acid gas was passed through it till it had no further effect. The liquid separated from the brown resinous mass that was formed had still an odour resembling that of cymol; when treated with fuming nitric acid, it gave a nitro-substitution product having the smell of bitter almonds. It had a refraction of 1·4661 for A at 19° C., and a dispersion of ·0287, numbers lower certainly than those obtained for cymol from oil of cumin, and from camphor, and throwing doubt on its identity with either of those forms of the hydrocarbon. It may be a product of the action of heat on the bark.

The oil that was capable of combination with hydrochloric acid was never separated in a pure state. Another liquid distilled over at a higher temperature: after repeated distillation, it retained the odour of Russia leather, but its boiling point was not constant.

Cajeput.—This oil, from the leaves or flower-buds of several species of *Melaleuca*, has been fully examined, especially by Max Schmidl, who finds it to consist almost entirely of a "bihydrate of cajputene" $C_{20}H_{18}O_2$.

Calamus.—From the bark of *Calamus aromaticus*. The two specimens of this oil had the same odour, and were slightly viscid. They did not boil till the temperature rose to 260° C., and consisted almost entirely of a hydrocarbon resembling that from oil of cubebs. Burnt with oxide of copper, 0·2685 grm. gave ·8630 carbonic acid and 0·2838 water, which give the following percentage proportions :—

	Experiment.	Calculated.
Carbon	87·66	88·23
Hydrogen ..	11·74	11·77
	99·40	100·00

Towards the end of the distillation, a small quantity of oil of a deep-blue colour distils over. This has happened in other cases also, and arises from the presence of an intensely blue body, more particularly described below under oil of wormwood.

Caraway.—The seeds of the *Carum Carvi* contain an essential oil, which has been frequently examined. It consists mainly of a hydrocarbon $C_{20}H_{16}$, named c a r v e n e, and an oxidized oil $C_{20}H_{14}O_2$ named c a r v o l. The carvol was identical, but the hydrocarbon differed slightly in its physical properties in the three specimens examined. This may arise from their being taken at different periods of the distillation.

Cascarilla.—From the bark of a species of *Croton.* It separated on fractional distillation into two hydrocarbons, having very different boiling points, the first with an odour of oil of lemon, and almost identical in physical properties with that hydrocarbon; the second almost identical with that derived from calamus.

Cassia.—This oil, derived from the outer bark of the *Laurus Cassia,* consists almost wholly of an oxidized oil which is said to be cinnamic aldehyde.

Cedar-wood.—This oil, from the shavings of *Juniperus virginiana,* obtained in making cedar pencils, was viscid, and began to distil only at 271° C., near which point the great bulk passed over. It contains oxygen.

Cedrat.—From the rind of the *Citrus Medica.* It consists almost entirely of a hydrocarbon similar to that from lemons.

Citronella.—This is produced from the leaves of the *Andropogon Schœnanthus.* The two specimens from Ceylon and from Penang both had the same agreeable odour, and consisted almost wholly of an oxidized oil of specific gravity ·8741 at 20° C., and boiling at 200° C.

Cloves.—The unexpanded flower-buds of the *Caryophyllus aromaticus* yield this oil, which has been previously well examined by B o n a s t r e and others. It contains a small quantity of a hydrocarbon, to which the formula $C_{30}H_{24}$ is assigned. The great bulk however is eugenic acid.

Coriander.—This oil is derived from the fruit of *Coriandrum sativum*. The specimen examined began to boil at 177° C., and between that point and 182° C. a liquid passed over in quantity, which on rectification from sodium was acted on destructively.

Cubebs.—The fruit of *Piper Cubeba* yields a viscid oil which when distilled from sodium boils at 260° C. and resembles the hydrocarbon from cloves. The specimen also contained a minute quantity of the blue substance already alluded to.

Dill.—From the seeds of *Anethum graveolens*. It contains a considerable quantity of a hydrocarbon which has a lemony odour and boils at 173° C, specific gravity ·8467. As the optical properties differed more than usual from those of turpentine, two combustions of this hydrocarbon were made.

I.—0·354 grm. burnt with oxide of copper, gave 1·1435 of carbonic acid and 0·3747 of water.

II.—0·336 grm. gave 1·0773 of carbonic acid and 0·353 of water.

These agree with the formula $C_{20}H_{16}$.

	I.	II.	Calculated.
Carbon	88·09	87·96	88·23
Hydrogen ..	11·76	11·74	11·77
	99·85	99·70	100·00

Elder.—The flowers of *Sambucus nigra* give a small quantity of an oil, my specimen of which was quite limpid, and of a pale yellow colour. It consisted principally of a hydrocarbon, closely resembling that just described.

0·4626 grm. burnt with oxide of copper, gave 1·493 of carbonic acid, and 0·4876 of water.

This shows it also to be $C_{20}H_{16}$.

	Experiment.	Calculated.
Carbon......	88·03	88·23
Hydrogen ..	11·72	11·77
	99·75	100·00

When this oil of elder was first heated, a little water and sulphuretted hydrogen came off. The residue in the retort, after the separation of the hydrocarbon, solidified, and consisted principally of a white solid substance, sparingly soluble in alcohol, very

soluble in ether, crystallising on evaporation; it is not soluble in potash or ammonia.

Eucalyptus amygdalina.—The oil, which exists in large quantity in the leaves of this tree, was found to consist chiefly of a hydrocarbon, analogous to turpentine, and resembling that liquid in its odour.

0·2692 grm. burnt with oxide of copper, gave 0·8708 of carbonic acid, and 0·2865 of water.

This agrees with the formula $C_{20}H_{16}$.

	Experiment.	Calculated.
Carbon	88·22	88·23
Hydrogen. . . .	11·82	11·77
	100·04	100·00

Eucalyptus oleosa.—The leaves of this tree or shrub yield an oil, the principle constituent of which resembles oil of cajeput in its physical properties.

Indian Geranium.—This oil seems to be the same as that termed elsewhere " East Indian Grass oil," which is said to be produced from *Andropogon Ivaracusa.* The specimen consisted of a mixture of liquids, from which it was found very difficult to isolate any one with a fixed boiling point.

Lavender.—From the flowers of *Lavandula vera.* This oil has been frequently examined, and is said to contain a hydrocarbon of the usual composition, and camphor; but it was difficult to separate these in the specimen examined.

Lemon.—The essential oil of the rind of *Citrus Limonum* has been fully examined by different chemists. It is principally composed of a hydrocarbon $C_{20}H_{16}$. Its purity cannot be depended on in England, and therefore I have examined no specimen except the one obtained direct from the Dominican Friars.

Lemon-grass.— The *Andropogon Nardus* yields this essential oil, which from its odour is frequently called oil of verbena. The two specimens examined, one from Ceylon, and the other from Penang, agreed in character, and appeared scarcely distinguishable from citronella.

Melaleuca ericifolia.—The oil distilled from the leaves of this plant closely resembles oil of cajeput.

Melaleuca linarifolia.—This oil, also from the leaves, is of the same general character as the preceding.

Mint.—*Mentha viridis* yields this oil, which was found to contain a hydrocarbon almost identical with oil of turpentine in odour and other physical properties, mixed with an oxidized oil, to which is due the peculiar smell of the plant. It boils at 225°C.; its specific gravity is 9·515, and it was found to be isomeric with carvol. It should therefore, by analogy, be called menthol.*

Myrtle.—Many parts of the *Myrtus communis* contain this oil. Three quarters of the specimen distilled over between 160°—176°C. leaving a reddish-brown residue, which evolved sulphuretted hydrogen. The distillate rectified as usual proved to be a hydrocarbon $C_{20}H_{16}$, of rather high specific gravity, with an odour resembling that of the hydrocarbon from bay.

0·3205 grm. burnt with oxide of copper yielded 1·0265 carbonic acid and 0·3340 water, which give the following percentage :—

	Experiment.	Calculated.
Carbon	87·68	88·23
Hydrogen. . . .	11·58	11·77
	99·26	100·00

Myrrh.—Procured by the distillation of the gum-resin from *Balsamodendron Myrrha.* The specimen was very viscid and dark, in colour brownish-green. It began to boil at about 266° C., giving an oxidized oil, which resinified very rapidly, and retained its greenish colour and strong smell of myrrh, after repeated rectification.

Neroli.—The essential oil of the flowers of *Citrus Aurantium.* The two specimens of this orange-flower oil were reddish-yellow, and when dissolved in alcohol gave a fluorescent solution, the surface-blue resembling that of quinine-salts, and being also produced mainly by the extreme rays of the spectrum. It was separated by distillation into two oils—the one boiling at 173° C., and closely resembling the hydrocarbon from bergamot, while the other, which appeared to be an oxidized oil, was not obtained with a fixed boiling point. The fluorescence, and the peculiar odour of the orange flower are due to the latter. It is slightly soluble in water.

Nutmeg.—From the seed of *Myristica aromatica.* The three

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* Dr. Oppenheim has suggested this as one of the new names of camphor of peppermint; but the other name *mentholic alcohol* is more consonant with his theory.

specimens examined consisted of varying proportions of a hydro-carbon resembling carvene, and an oxidized oil with the boiling point 224° C., and sp. gr. ·9466. As it closely resembles carvol and menthol in its properties, it may by analogy be named myristicol.

0·406 grm. of the hydrocarbon yielded 1·3074 grm. carbonic acid, and 0·435 grm. water.

	Experiment.	Calculated.
Carbon	87·81	88·23
Hydrogen ..	11·90	11·77
	99·71	100·00

Orange-peel.—The oil contained in the peel of *Citrus Aurantium* is known to consist almost entirely of a hydrocarbon of the usual type, which has been named Hesperidene. A small quantity of a solid crystalline substance was also obtained.

Parsley.—From the seeds of *Apium Petroselinum.* The crude oil was viscid, and of a brownish-green colour. It contained a small quantity of a hydrocarbon of the usual composition; but there remained in the retort a much larger amount of a brown resin insoluble in potash, with a very disagreeable smell.

Patchouli.—This very powerful and characteristic odour is de-rived from the leaves and stems of *Pogostemon Patchouli* (Lindley) or *Plectranthus crassifolius* (Burnett). Both the Indian and Penang specimens were brownish-yellow, and slightly viscid. They began to boil only at 257° C., at which temperature nearly all distilled over, but towards the end the thermometer rose much higher, and the distillate contained the blue substance already noticed. That which passed over previously was found to be a hydrocarbon analogous to that from cubebs.

Peppermint.—This is obtained by distilling *Mentha Piperita.* Both the English and Italian specimens were found to contain a hydrocarbon, which could be separated from the oxidized com-pounds by means of sodium. It had physical properties differing little from those of the hydrocarbon from bay. No solid camphor was obtained from either.

The solid camphor of peppermint has been fully described by Oppenheim. Its optical properties, when melted, may be found in Phil. Trans., 1863, p. 341. The following comparison has also been made :—

	Temp.	Sp. gr.	Refr. D.
Solid camphor	16°	0·9383	1·5070 (about)
Melted camphor ..	43°	0·8786	1·4505

Petit Grain.—Under this name is sold an oil derived from the leaves and young unripe fruit of the orange-tree. It consists mainly of a hydrocarbon, probably identical with that from oil of neroli.

Rose.—This essential oil, or otto as it is termed, is obtained from the flowers of *Rosa centifolia*. It is a solution of a solid crystallizable body in an oxidized oil, which has a boiling point of 216° C., and a specific gravity 881 at 20° C.; crystals of the other constituent may be generally seen floating about in the oil, especially in cold weather. This solid is said to be a hydrocarbon. It is only slightly soluble in alcohol, which affords the means of completely separating the oil from it, but it has a great power of condensing ether vapour, and thus forming an ethereal solution.

Rosemary.—From the *Rosmarinus officinalis*. The oil was found to consist almost wholly of a hydrocarbon resembling that from myrtle.

Rosewood.—Obtained from the wood of *Convolvulus scoparius*. This oil was slightly viscid, and did not boil till the temperature reached 249° C., at which temperature four-fifths passed over. The rectified oil had an odour suggesting that of roses and santalwood, and on combustion proved to be of the usual composition. 0·377 grm. gave 1·209 of carbonic acid, and 0·3963 of water.

	Experiment.	Calculated.
Carbon......	87·46	88·23
Hydrogen ..	11·68	11·77
	99·14	100·00

This oil is sometimes called by the name of *Rhodium*.

Santal-wood.—Distilled from the wood of *Santalum album*. The oil is viscid and yellow; on fractional distillation, it nearly all passes over at 293° C., giving a liquid which contains oxygen.

Thyme.—This oil from the *Thymus Serpyllum* is deep red in colour. The specimen examined was principally composed of a hydrocarbon like that of turpentine. It contained little if any of the thymol, $C_{20}H_{14}O_2$, which has been described by Doveri and Lallemand, as occurring in this essential oil. The hydrocarbon has been named thymene.

Turpentine.—This oil, from various species of *Pinus* has been the subject of innumerable researches. It is well known to consist of a hydrocarbon $C_{20}H_{16}$, holding in solution resins produced by oxidation.

Verbena.—From the *Aloysia citriodora*. The specimen was red in colour ; on distillation it yielded an oxidized oil similar to that from lemon-grass, which is often called in commerce "Verbena," from the analogy of its odour. A large proportion of resinized products was left in the retort, and evolved sulphuretted hydrogen when heated.

Winter-green.—The leaves of *Gaultheria procumbens* yield this oil, which has been examined by Cahours. It contains a small quantity of a hydrocarbon of the usual composition, named gaultherilene, and a large proportion of another liquid which is salicylate of methyl.

Wormwood.—From *Artemisia Absinthium.* The oil had a dark greenish-brown colour. On distillation, it yielded a hydrocarbon like turpentine, an oxidized oil said by Leblanc to be $C_{20}H_{16}O_2$, and the blue substance already referred to.

The specimen from Hamburg contained a considerable amount of this blue body, which distils over with the last portions, and
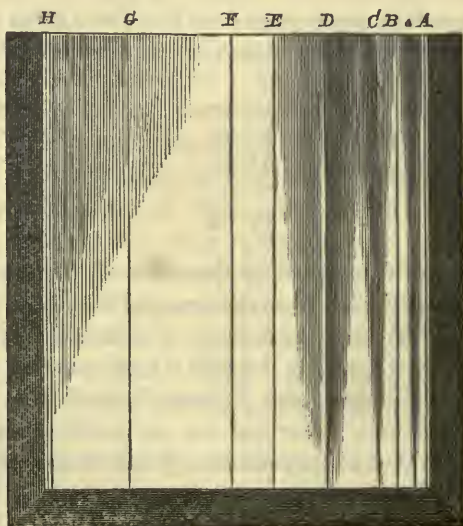
which I have not yet succeeded in separating from the oils of high boiling point that have always accompanied it. It appears not to be attacked by sodium, but at each distillation it diminishes in quantity, and leaves a resinous mass in the retort. It dissolves in ether, alcohol, benzol, and essential oils. Its solution in alcohol is neutral to test-paper. When burnt with soda-lime it evolved ammonia, but when decomposed with fuming nitric acid it gave no trace of sulphuric acid. It has a most intense colour, appearing almost black when as pure as I have succeeded in obtaining it. Its solution in oils or alcohol, when examined by means of the hollow wedge and prism, gives the very characteristic spectrum represented in the annexed diagram. It first absorbs the orange-yellow rays near D, and afterwards the greenish-yellow, and the orange at C. At a particular depth it transmits the red rays anterior to A, absorbs those between a little beyond A and *a*, transmits the red from *a* to about C, where a dark band occurs, and thence again to about midway between C and D. From this point to D there seems to be complete absorption, then a bright space followed by a darkening of the greenish rays, but it is clear again from about E till we approach G, beyond which line little light is transmitted. At a greater depth nothing is suffered to pass, except the greenish-blue rays, and the extreme red-band. Acids and alkalis alter the colour greatly, converting it generally into a green.

It is proposed to give this blue neutral colouring matter the name of c œ r u l e i n.

Since the above was written, Mr. Piesse has sent to the Chemical Society a short description of this blue oil, and Dr. Gilbert, hearing that I was engaged on the subject, kindly offered me two fine specimens which had been prepared for him twenty-three years ago, and were still magnificently blue. On distilling that from *Matricaria Chamomilla*, I was able to separate and purify a small quantity of a hydrocarbon, with boiling point and optical properties like those of the hydrocarbon from lemon or dill, while at the same time there began to pass over an oxi-dized oil, the boiling point of which seemed to lie somewhere about 200° C., but it was never obtained free from cœrulein; on con-tinuing the distillation, a more and more intensely blue oil came over, the thermometer rising above 320°, when there was left in the retort a brown resin insoluble in alcohol, but very soluble in ether. On repeated distillation, the blue compound was more and

more concentrated, but the boiling point always had a considerable range.

As yet I have not succeeded in devising any means of ascertaining whether the blue oil thus obtained was almost pure cœrulein, or whether it was mainly an oil of high boiling point holding in solution some of the colouring matter; but my opinion inclines to the latter view, principally on this ground : if a portion of the distillate which passed over at a high temperature but is not very blue, be treated with sodium, a strong action ensues, and a more volatile colourless oil is produced, having a peculiar odour suggesting that of rue. Now, if a portion of the most concentrated blue liquid be cohobated with sodium, the same oil apparently is produced in considerable quantity.

The most concentrated blue oil obtained from this source agreed with the blue substance described above in every particular, excepting that it was not turned green by dilute acids and alkalis.

Its odour resembles that of caoutchine; it dissolves readily in glacial acetic acid, and in bisulphide of carbon; it is not decolorized by sulphurous acid, sulphuretted hydrogen, or brominewater; it does not attach itself to animal charcoal, nor does it dye wool, cotton, or silk. It gave the following refractive indices :—

Temperature.	Red band.	Blue band.
9°C.	1·5076	1·5330

The specimen from *Achillea millefolium* yielded a similar blue oil, distilling over at a very high temperature, and a resin containing a substance that was insoluble in alcohol, but soluble in ether, from which it could be obtained in tufts of crystals on evaporation. This blue substance was clearly the same as that from other plants.* Like them it gave indications of ammonia, or some volatile alkali, when it was heated with soda-lime, but the intensely blue oil yielded, in each instance, little more than a trace. It is hard to say whether this is to be attributed to the nitrogenized body being present in very small quantity, or to the difficulty of decomposing it. When special precautions were taken, a portion of blue oil was still found to escape destruction,

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* Sir David Brewster examined these specimens of Dr. Gilbert's optically many years ago, and noticed the absorption at *a*.

and to condense in the small tube of the hydrochloric acid appa-
ratus. When diluted with a hydrocarbon, this blue substance
may be distilled from sodium, but it is slowly attacked by it even
at the ordinary temperature.

Mr. Piesse calls this blue oil *azulene;* but the name azuline has
long been appropriated to one of the colouring matters derived
from coal-tar. I am told that there is a blue pigment prepared
by Winsor and Newton which is known as cœrulein.

I hope to revert to this subject if fortunate enough to get a suf-
ficiency of the blue oil.

THE HYDROCARBONS.

From the preceding descriptions it appears that there exists a
hydrocarbon of the formula $C_{20}H_{16}$, or some multiple of that, in
the essential oils of anise, bay, bergamot, calamus, caraway,
cedrat, cloves, cubebs, dill, elder, Eucalyptus amygdalina, lemon,
myrtle, neroli, nutmeg, orange-peel, parsley, rosemary, rosewood,
thyme, turpentine, and wintergreen; and the oils of cascarilla,
mint, patchouli, peppermint, and wormwood, contain hydro-
carbons, which resemble so closely some of the preceding in their
physical properties, that an ultimate analysis by combustion
seemed unnecessary to establish their composition.

The following Table gives several physical properties of these
hydrocarbons after they had been frequently rectified from sodium.
Dr. Stenhouse's laurel-turpentine is added to the list, and so
are samples of colophene and terebene. They are arranged
according to their specific gravities at 20° C. The column headed
"Dispersion at 20° C." gives the difference between the refractive
indices of the lines H and A. The sensitiveness is the amount of
diminution of the refractive index when the temperature rises
10° C.; it is calculated for the line A, and the number 48 is a
short expression for 0·0048 (see Phil. Trans. 1863, p. 325). The
"specific refractive energy" is the refractive index, minus unity,
divided by the density. In the present table it is taken for A:
that is, the column represents $\frac{\mu_A - 1}{D}$

Source of hydrocarbon.	Specific gravity at 20° C.	Boiling point.	Refractive index A, at 20° C.	Dispersion at 20° C.	Sensitiveness.	Specific refractive energy.	Rotation.
Orange-peel	·8460	174°C	1·4645	·0277	48	·5490	+ 154
,, Florence......	·8468	174°	1·4650	·0281	49	·5491	+ 260
Cedrat..................	·8466	173°	1·4650	·0280	49	·5492	+ 180
Lemon..................	·8468	173°	1·4660	·0280	49	·5502	+ 172
Bergamot	·8466	175°	1·4619	·0295	49	·5456	+ 76
,, Florence	·8464	176°	1·4602	·0287	48	·5437	+ 82
Neroli..................	·8466	173°	1·4614	·0291	47	·5450	+ 76
Petit grain	·8470	174°	1·4617	·0282	46	·5439	+ 60
Caraway, Hamburg, 1st dist.	·8466	176°	1·4645	·0286	48	·5486	+ 180
Dill	·8467	173°	1·4646	·0288	46	·5486	+ 242
Cascarilla	·8467	172°	1·4652	·0305	49	·5494	0
Elder	·8468	172°	1·4631	·0269	47	·5468	+ 15
Bay	·8508	171°	1·4542	·0260	47	·5338	− 22
Gaultherilene...........	·8510	168°	1·4614	·0271	49	·5422	..
Nutmeg	·8518	167°	1·4630	·0284	47	·5435	+ 49
,, Penang..........	·8527	166°	1·4634	·0274	49	·5434	+ 4
Carvene................	·8530	166°	1·4610	·0261	48	·5440	− 20
,, Hamburg, 2nd dist.	·8545	..	1·4641	·0263	48	·5431	+ 86
Wormwood.............	·8565	160°	1·4590	·0253	47	·5359	+ 46
Terebene...............	·8583	160°	1·4670	·0275	48	·5440	0
Anise	·8580	160°	1·4607	·0268	47	·5368	..
Mint	·8600	160°	1·4622	·0255	48	·5374	+ 30
Peppermint	·8602	175°	1·4577	·0267	47	·5321	− 60
Laurel turpentine	·8618	160°	1·4637	0260	47	·5380	+ 94
Thyme....	·8635	160°	1·4617	·0282	48	·5346	− 75
Turpentine I	·8644	160°	1·4612	·0250	47	·5335	+ 48
,, II............	·8555	160°	1·4590	·0256	47	·5365	− 87
,, III	·8614	160°	1·4621	·0249	..	·5364	− 90
Turpentine IV	·8600	160°	1·4613	·0254	47	·5364	− 88
Eucalyptus amygdalina ..	·8642	171°	1·4696	·0323	49	·5434	− 142
Myrtle..................	·8690	163°	1·4565	·0248	47	·5253	+ 64
Parsley	·8732	160°	1·4665	·0291	46	·5355	− 44
Rosemary	·8805	163°	1·4583	·0241	46	·5205	+ 8
Cloves..................	·9041	249°	1·4898	·0284	45	·5417	..
Rosewood	·9042	249°	1·4878	·0277	45	·5395	− 11
Cubebs	·9062	260°	1·4950	·0302	41	·5462	+ 59
Calamus	·9180	260°	1·4930	·0322	42	·5370	+ 55
,, Hamburg	·9275	260°	1·4976	·0337	43	·5365	+ 22
Cascarilla	·9212	254°	1·4926	·0307	42	·5347	+ 72
Patchouli	·9211	254°	1·4966	·0274	42	·5391	..
,, Penang	·9278	257°	1·4963	·0275	44	·5349	− 90
,, French	·9255	260°	1·5009	0262	42	·5412	..
Colophene	·9391	315°	1·5084	·0309	41	·5413	0

It will be seen at once that these hydrocarbons divide themselves into two great groups, the line of separation being between those from rosemary and cloves. The first group, with a lower specific gravity, has always a far lower boiling point, a smaller

index of refraction, and a higher sensitiveness. It has also on the whole a smaller dispersion. The specific refractive energy, however, of the two groups is about the same. It may also be noted generally of the hydrocarbons of the first group, that they are more limpid, and dissolve more freely in aqueous alcohol.

And these large groups are capable of subdivision. The first ten hydrocarbons in the Table resemble one another very closely. Indeed, it is probable that the three which are derived from the peel of the orange, citron, and lemon respectively, should be considered as identical rather than isomeric; and it is not unlikely that some of the others are the same body from different plants. Gaultherilene, carvene, and the hydrocarbon from nutmeg, form a small group, if indeed they are not identical. The hydrocarbons from wormwood, anise, thyme, mint, and laurel turpentine, group with ordinary turpentine; bay, myrtle, and rosemary stand alone, each having a low refraction and dispersion, but they differ much in specific gravity. Peppermint is somewhat intermediate in its properties. Terebene and the hydrocarbons from parsley and Eucalyptus amygdalina give high refractive indices. It is possible that some of these last contain a small quantity of some hydrocarbon of another type, but nearly the same composition.

Again, the second large group with the higher specific gravities is capable of subdivision. The hydrocarbons from cloves and rosewood appear nearly, if not quite, identical in properties, and are certainly different from patchouli, calamus, and cascarilla.

Colophene differs from the second large group in much the same way as that differs from the first, though to a smaller extent.

All the members of the first great group, with the boiling points included between 160° and 176°C., will have the formula $C_{20}H_{16}$, which is usually assigned to oil of turpentine on the ground of its vapour-density, and compounds with the hydracids.

All the members of the second great group, with boiling points included between 249° and 260°C., will have the formula $C_{30}H_{24}$, which is assigned to oil of cubebs from its compound with hydrochloric acid.

Colophene, with a boiling point of 315°C., has long had the formula $C_{40}H_{32}$ assigned to it.

The specific refractive energy is a property of bodies intimately connected with their ultimate composition, and it might be expected that, notwithstanding diversities of boiling point and density, this property would be the same for the different isomeric

hydrocarbons. Yet though the differences are not great, they seem to be real, for the lemon group is uniformly about ·549, and the turpentine group about ·536.

Nor are these differences diminished, if we reckon the specific refractive energy, not for the line A, but for the theoretical limit of the spectrum, so as to get rid of the influence of dispersion as much as possible. The following table gives the calculation for six hydrocarbons, which may be considered typical ones :

Source of hydrocarbon.	Spec. refr. energy of limit.
Orange-peel.	·5385
Nutmeg.	·5335
Turpentine.	·5272
Cloves.	·5346
Calamus.	·5264
Colophene.	·5314

It is worthy of remark that this property forms no distinction between the three great groups, the specific refractive energies of the hydrocarbons from nutmeg and cloves being practically the same, and closely resembling that of colophene.

There can be no doubt that hydrocarbons exist isomeric with oil of turpentine, but having a boiling point of 173°C., or thereabouts, and a specific gravity of ·846, but it is just conceivable that the higher refraction of the lemon group may, after all, be due to the presence of a small quantity of some body containing a larger proportion of carbon, and which cannot be separated by distillation, a suspicion that the recorded ultimate analyses rather tend to support.

In this classification of isomeric hydrocarbons no regard has been paid to the phenomena of circular polarization. This has arisen from the fact that different samples of the same hydrocarbon resembling one another closely in every other physical property, frequently differ in this. The above Table affords several instances. We need not be astonished, therefore, at wide differences between hydrocarbons, which, in other respects, are closely analogous, but which are derived from different species or genera of plants. Yet on looking down the column we can hardly fail to remark that the great lemon group is characterized by the highest

numbers, and that they are always + or right-handed, with the exception of the hydrocarbon from cascarilla which belongs to this group, and actually has no influence at all on the plane of polarization.

The pure hydrocarbons have rarely powerful odours, and it is often difficult to remove every trace of the oxidized compounds, to which the characteristic fragrance of the essential oils is generally due. Yet the odour of these liquids affords some support to the classification founded on other properties. Those which have the specific gravity 0·846 emit a more or less lemony odour when freshly distilled, and some of those which resemble closely oil of turpentine in their general characters, resemble it also in this respect.

As this communication has already extended to a considerable length, my observations on the oxidized oils will be reserved for some future occasion, when I hope also to enter more fully into the chemical and physical history of some of these hydrocarbons.
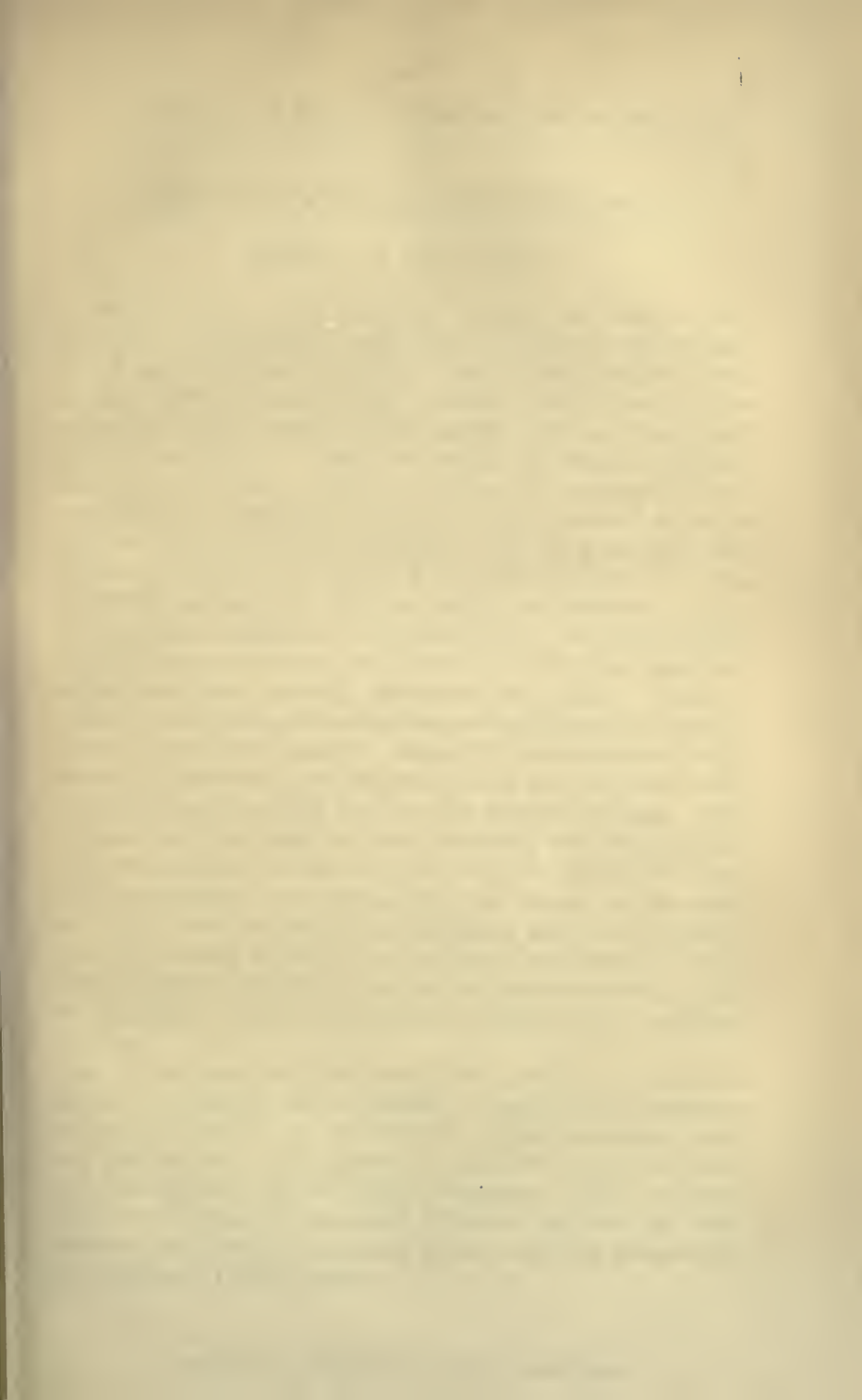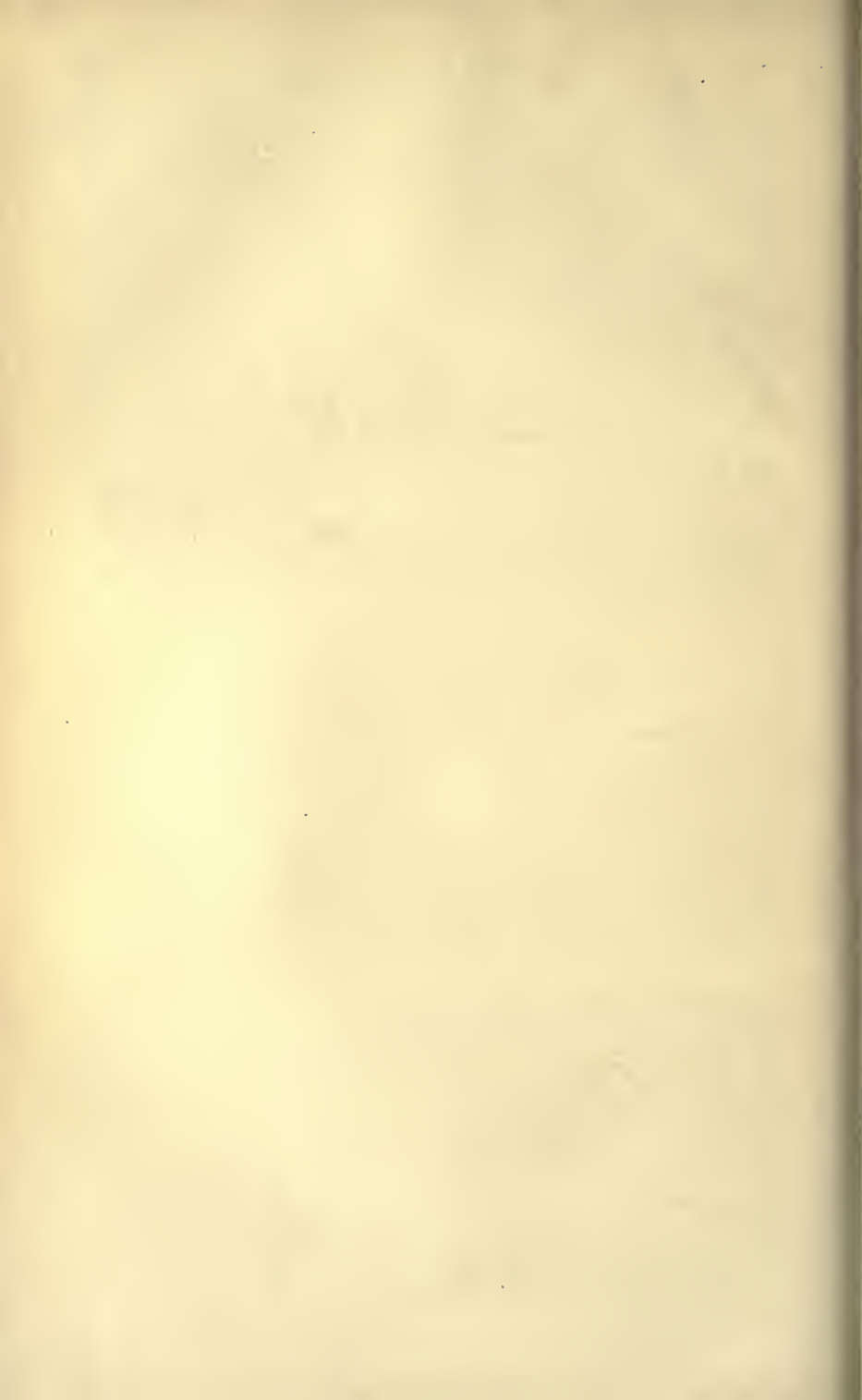
NOTE ON CRYSTALLISED GLYCERIN.

By Dr. J. H. GLADSTONE.

AT the meeting of the Chemical Society, on January 17, Dr. Squire exhibited a large mass of crystals, which had formed part of 5 tons of glycerin that he had received from Germany during the very cold weather of last January. He stated that these crystals slowly melted into good ordinary glycerin containing a small percentage of water; and that when they had once melted, he had never succeeded in re-crystallising the substance, though he had exposed it to long-continued and great cold, had shaken it at the same time, and had immersed unmelted crystals in the cooled liquid.

After the meeting Dr. Squire kindly gave me two or three ounces of these crystals in a corked bottle. They looked very like loaf-sugar which had been moistened with water, and was disintegrated and partially dissolved into syrup. When I reached home, finding the specimen was melting rather rapidly, I put it outside the window. Snow fell that night, and in the morning it appeared to me that there were more crystals inside the bottle than there had been on the previous evening. The specimen was then taken to the laboratory, and being placed on the mantel-piece, in two or three days the crystals had very nearly disappeared, but on removing the bottle to the other end of the room, they began to form again, and in the course of a few days nearly the whole had become a solid mass of trans-parent crystals. After this they melted again completely; and the liquid then resisted a temperature of about $-18°$ C. without freezing.

As it was said that this remarkable specimen of glycerin contained sulphoglycerate of sodium, a portion was heated in a platinum crucible. It distilled off, without blackening, until very near the end of the operation, and left an ash weighing only 0·37 per cent. of the original substance. This consisted mainly of alkaline sulphates and chlorides, and from its small quantity can hardly be supposed to have had any influence on the formation of the crystals.

On a Law in Chemical Dynamics. By JOHN HALL GLADSTONE, Ph.D.,
F.R.S., and ALFRED TRIBE, F.C.S.

(Abstract.)

IT is well known that one metal has the power of decomposing the salts
of certain other metals, and that the chemical change will proceed until
the more powerful metal has entirely taken the place of the other.   The
authors have investigated what takes place during the process.

The experiments were generally performed as follows :—72 cubic centi-
metres of an aqueous solution of the salt of known strength, and at 12°
Centigrade, were placed in a tall glass ; a perfectly clean plate of metal of
3230 square millimetres was weighed and placed vertically in this solution
without reaching either to the top or bottom ; the action was allowed to
proceed quietly for ten minutes, when the plate was removed, and the de-
posited metal was washed off.   The loss of weight gave the amount of
metal dissolved, and represented the chemical action.

The most complete series of results was with copper and nitrate of silver.

Nitrate-of-silver solution.		Copper dissolved.			Theo-retical.	Differ-ence.
Propor-tional number.	Percentage of salt.	Actual weights.		Average.		
1.	0·3541	0·0045, 0·0050		0·00475	0·00455	+0·0002
2.	0·7083	0·0135, 0·0140		0·01375	0·01365	+0·0001
3.	1·0623	0·0240, 0·0250		0·0245	0·0259	−0·0014
4.	1·4166	0·0420		0·0420	0·0409	+0·0011
5.	1·7705	0·0600		0·0600	0·0583	+0·0017
6.	2·1246	0·0785		0·0785	0·0790	−0·0005
7.	2·4788	0·0975		0·0975	0·0994	−0·0019
8.	2·8332	0·1230, 0·1230		0·1230	0·1228	+0·0002
9.	3·1873	0·1510, 0·1480		0·1495	0·1481	+0·0014
10.	3·5415	0·1680, 0·1670		0·1675	0·1749	−0·0074
11.	3·8956	0·1955		0·1955	0·2035	−0·0080
12.	4·2497	0·2170, 0·2285, 0·2310, 0·2200		0·2241	0·2336	−0·0095
14.	4·9580	0·2740		0·2740	0·2982	−0·0242
16.	5·6664	0·3270		0·3270		
20.	7·0830	0·4540, 0·4100		0·4320		
24.	8·4994	0·5400		0·5400		
30.	10·624	0·6850		0·6850		
32.	11·333	0·7100		0·7100		
40.	14·166	0·8440, 0·9090		0·8765		
48.	16·999	1·0690		1·0690		
60.	21·246	1·359		1·359		
70.	24·788	1·580		1·580		

In the earlier terms of this series, *twice the percentage of silver-salt gives
three times the chemical action*.   The mathematical expression of this law is
$c = C\, p^{\frac{\log 3}{\log 2}}$, c being the chemical action, C the constant, and p the propor-
tionate quantity of salt.   The close agreement of the observed num-
bers with those calculated on this supposition as far as the 9th term

is shown in the 5th and 6th columns. The law then breaks down, and after about 7 per cent. the increased action is almost in direct ratio with the increased strength.

The position of the plate in the solution was found to make no difference to this 2–3 law.

Similar series of experiments were made with zinc and chloride of copper, zinc and sulphate of copper, zinc and nitrate of lead, iron and sulphate of copper, and other combinations ; and in every instance where the solution was weak and the action simple, the law of three times the chemical change for twice the strength was found to hold good.

It was proved that the breaking down of the law at about 3·5 per cent. of salt in solution was irrespective of the quantity of the liquid, or of the time for which the plate was exposed. With 72 cub. centims. of a 1·41 per cent. solution of nitrate of silver the rate of action remained sensibly the same for as long as twenty-five minutes, notwithstanding the constant deposition of silver. This apparently paradoxical result is due to fresh relays of the original solution being brought up to the plate by the currents produced, and that period of time elapsing before any of the products of decomposition are brought back again in their circuit.

When it was perceived that within easily ascertainable limits the chemical action is the same for similar consecutive periods of time, experiments were made in far weaker solutions. It was only necessary to lengthen the time of exposure. It was thus found that the law of three times the chemical action for twice the strength of solution holds good through at least eleven terms of the powers of 2 ; in fact, from a solution that could dissolve one gramme of copper during the hour, to a solution that dissolved only 0·000001 gramme, a million times less.

The manner in which the silver is deposited on a copper plate was examined, and the currents produced were studied. At first a light blue current is perceived flowing upwards from the surface of the plate, presently a deep blue current pours downwards, and these two currents in opposite directions continue to form simultaneously. A similar phenomenon was observed in every case where a metallic salt attacked a plate of another metal. The downward current was found to be a solution of almost pure nitrate of copper, containing about three times as much NO_3 as the original silver solution, while the upward current was a diluted solution of the mixed nitrates. Moreover the heavy current took its rise in the entangled mass of crystals right against the plate, while the light current flowed from the tops of the crystalline branches. It was evident that when the fresh silver was deposited on these branches, and the fresh copper taken up from the plate, there was not merely a transference of the nitric element from one combination to another, but an actual molecular movement of it towards the copper plate, producing an accumulation of nitrate of copper there, and a corresponding loss of salt in the liquid that is drawn within the influence of the branching crystals. Hence the opposite currents.

The amount of action in a circuit of two metals and a saline solution must have as one of its regulating conditions the conducting-power of that solution. It appeared by experiment that a strong solution of nitrate of silver offers less resistance than a weak one; and it was also found, on adding nitrate of potassium to the nitrate of silver, that its power of attacking the copper plate was increased, that the augmentation of the foreign salt increased the action still further, and that the 2–3 law holds good between two solutions in which both the silver and potassium salt are doubled, though it does not hold good if the quantity of foreign salt be kept constant. Similar results were obtained with mixed nitrates of silver and copper.

While these later experiments offer an explanation of the fact that a solution of double the strength produces more than double the chemical action, they do not explain why it should produce exactly three times the effect, or why the ratio should be the same in all substitutions of this nature hitherto tried. The simplicity and wide range of the 2–3 law seem to indicate that it is a very primary one in chemical dynamics.

ON ESSENTIAL OILS. PART II.

By J. H. GLADSTONE, Ph.D., F.R.S.

EIGHT years ago I communicated a paper on Essential Oils to the Chemical Society, and in concluding it I promised a further communication, with experiments on the oxidised oils, and a fuller account of the chemical and physical history of some of the hydrocarbons. Shortly after the paper was printed, a series of unforeseen events took me almost wholly away from my laboratory; other scientific enquiries then engrossed my thoughts; and so the research on these essential oils was long laid aside. Now, however, I will endeavour to fulfil my promise, though not to carry out my whole design.

Before entering on any new observations, I wish to refer to some criticisms on my paper which Mr. Daniel Hanbury kindly sent me. They relate to the plants from which the oils are derived; and, as I know little of the subject myself, I will just place his statements against those of Mr. Piesse, on whose authority each of the controverted names was given.

Oil of calamus is distilled, not from *Calamus aromaticus*, but from the rhizome of *Acorus Calamus*.

Indian geranium oil is yielded by *Andropogon Pachnodes*.

The wild thyme of our heaths, *Thymus Serpyllum*, gives an essential oil, but the oil of thyme of commerce is from *Thymus vulgaris*.

During the past spring I was furnished by Mr. Piesse with specimens of some rare essential oils, not previously examined—those of citron, lign aloes, pimento, and vitivert.

The following were the determinations of the specific gravity and refraction of these oils as they came into my hands:—

Crude oils.	Specific gravity.	Temp. Cent.	Refractive indices.		
			A.	D.	H.
Citron	0·8914	10°	1·4729	1·4797	1·5011 ?
Lign aloes	0·8702	18°	1·4620	1·4679	
Pimento	1·0374	10°	1·5229	1·5325	1·5660 ?
Vitivert	1·0070	19·5°	1·5147	1·5218	

Citron.—This oil is obtained from the leaves of the lemon, *Citrus Limonum.* It was slightly yellow. It began to boil at 155° C., but the bulk consisted of a liquid having the boiling point 166°—168°; the specific gravity 0·8549 at 19·5°; the refractive index for A, 1·4680; and the dispersion 0·273. Its odour resembled that of lemon, and it was probably identical with the hydrocarbon found in other parts of the same plant.

Lign Aloes.—This is a colourless oil, with a characteristic pleasant odour, believed to be obtained from the wood of a large tree that grows in Mexico.* The principal part distils over at somewhere about 200°, but it seemed impossible by fractional distillation, even with the aid of sodium, to obtain a body of a fixed boiling point. The specific gravity and optical properties of the best rectified oil are given later on in this paper; they will be found to resemble closely the properties of citronellole, suggesting the idea that the principal constituent may also have the composition $C_{10}H_{16}O$.

Pimento.—This pungent oil is derived from the seeds of *Myrtus Pimenta.* It began to boil at about 197°, and the thermometer rose gradually to 242°, about which temperature the greater portion passed into the receiver. The first portion consists partly of an oil insoluble in potash; the second is wholly dissolved by an alkali. When rectified, though perhaps not quite pure, it was found to have the boiling point 243°; specific gravity at 12·5°, 1·0436; refractive index for A 1·5281; and dispersion about 0·416. Its odour was that of eugenic acid, and like that body it was freely soluble in potash, giving two salts, of which that which contains the larger proportion of acid will separate from a moderately strong solution in crystalline masses. As the physical properties mentioned above accord sufficiently well with those previously determined for eugenic acid,† there can scarcely be a doubt that oil of pimento is substantially the

* The Lign aloes of the sacred Scriptures is supposed to be the *Aquilaria Agallochum* of Northern India.
† Phil. Trans., 1863, p. 317.

same as oil of cloves, while each contains a small proportion of a hydro-carbon, to which is due the difference of their odours.*

Vitivert.—The crude oil was very viscid, of a dark brown colour, with an odour suggesting both santal wood and patchouli. On repeated distillations it was found to consist mainly of a liquid boiling at 280°—283°, but the action of sodium showed that this was a mixture of two bodies, the one decomposible and the other unalterable by that metal. The rectified oils were of a brownish-green colour on being freshly distilled, and changed to a truer green shortly afterwards —a circumstance which I have not observed in any other case. An examination of the hydrocarbon is given below, and confirms the close resemblance of this oil to those of cedar and santal wood.

THE HYDROCARBONS.

These are all of the composition $C_{10}H_{16}$, or a multiple of that. In the previous paper I described several new ones, of which I analysed eight. No names were given them beyond that of the oil from which they were obtained, but now, in accordance with the usual practice, I would suggest the following :—

Hydrocarbon from Bay .... Laurylene.
      ,,   ,, Calamus .... Calamene.
      ,,   ,, Dill .... Anethene.
      ,,   ,, Elder................. Sambucene.
      ,,   ,, Eucalyptus amygdalina .. Eucalyptene.
      ,,   ,, Myrtle .... Myrtene.
      ,,   ,, . Nutmeg .... Myristicene.
      ,,   ,, Rosewood .... Rhodiene.

Polymeric Groups.

When treating of the hydrocarbons of the essential oils in my previous paper, I distinguished between three polymeric groups, to which were assigned the formulæ $C_{10}H_{16}$, $C_{15}H_{24}$, and $C_{20}H_{32}$. The first group was said to comprise the great mass of these hydrocarbons—turpentine, orange, caraway, nutmeg, anise, thyme, myrtle, and twenty others ; the second, those derived from cloves, rosewood, cubebs, calamus, cascarilla, and patchouli ; while the third group was represented by colophene.

That colophene also has its isomerides is rendered probable by the descriptions given of paracajputene, and of the substances from other

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* Since writing the above, I find the same conclusion had been previously arrived at by Oeser.

sources which have been named colophene, but which are probably not identical with it.

If there is this distinction, the vapour-densities of members of the three groups should be different. Now the densities of oil of turpentine, pepper, juniper, elemi, lemon, and orange, together with gaultherylene, valerene, citrene, terebene, carvene, and caoutchene had been determined by various experimenters to be about, though generally a little above, the theoretical density for $C_{10}H_{16}$, viz., 4·71. The experimental density of colophene given in Gmelin's Handbook exceeds what would be required by $C_{20}H_{32}$. No member of the second group, however, had been examined in this respect, unless it be cedrene, which appears to belong to it, and which gave, according to Walter, the vapour density 7·5. $C_{15}H_{24}$ requires 7·06. I took the oils of patchouli and calamus.

	Calamene.	Patchouli.
Difference between weight of air and vapour	·3327 grm.	·311 grm.
Temperature of balance case	12·5° C.	9° C.
Temperature of sealing	280° C.	294° C.
Capacity of globe................	110·8 c.c.	98·49 c.c.
Residual air	2·6 c.c.	1·95 c.c.
Calculated density of vapour......	6·80	7·2

Each of these differs little from the theoretical 7·06, and they differ in opposite directions.

It is well known that several oils of the first group form compounds with hydrochloric acid of the composition $C_{10}H_{16}.2HCl$. It might therefore be anticipated that the oils of the second group would combine with a smaller quantity of hydrochloric acid; and indeed the hydrochloride of cubebene is said to be $C_{15}H_{24}.2HCl$. I tried patchouli and rhodiene. Dry hydrochloric acid gas was passed through the oil till it was perfectly saturated; in each case it remained liquid; portions were freed from excess of acid by exposure in vacuo over sticks of potash, or by heating in a water-bath, and analysed. Two different preparations from patchouli gave 7·11 and 11·18 per cent. of chlorine; the product from rhodiene purified in the two ways mentioned above gave 18·26 and 16·78 per cent. These numbers differ from one another, and from those deduced from any probable formula. They seem to indicate that these liquid hydrochlorides are somewhat indefinite.

The compound of colophene with the acid gas was similarly formed and examined. It was very viscid, and of a dirty brown rather than an indigo colour, as previously described. It lost nearly all this colour, together with the smell of hydrochloric acid, when heated in a water-bath or exposed over potash in vacuo; but it still retained some chlo-

rine, a very little however, for analysis showed only 1·76 per cent. in the first instance and 2·01 per cent. in the second. If we suppose the whole of the colophene combined with this hydrochloric acid we should arrive at the very improbable formula of nothing less than $C_{120}H_{192}HCl$. The power of HCl to combine with these hydrocarbons evidently becomes greatly diminished as their molecules become more complex.

The hydrocarbons of the first group, derived from oil of turpentine, orange-peel, cedrat, and thyme were found to require from 5·3 to 5·6 volumes of slightly diluted methylated spirit to dissolve them; while the hydrocarbons of the second group, from oils of calamus, cubebs, patchouli, and rosewood, required from 27 to 30 volumes. Colophene and paracajputene are almost, if not wholly, insoluble in aqueous alcohol.

It is well known that strong sulphuric acid acts powerfully on oil of turpentine, giving rise to two new isomeric compounds, terebene and colophene. It was found to have a similar action on the hydrocarbon from nutmeg; but when a member of the second group was submitted to its action, nothing analogous to colophene was produced.

Another distinction between the groups is a small but clearly recognizable difference in their expansibility by heat. On referring to my former paper it will be seen that the "sensitiveness" of the first group varies from 46 to 49, while that of the second group never exceeds 45, and averages 43. Colophene is only 41. In connection with this matter the following determinations were made of the expansion of oil of turpentine by heat:—

Oil of Turpentine.

Temperature.	Specific gravity.	Expansion for 5° C.
15° C.	0·8665	—
20°	0·8632	0·0033
25°	0·8599	0·0033
30°	0·8565	0·0034
35°	0·8531	0·0034
45°	0·8464	0·00335

Oil of rosewood was found to expand 0·00321 or 0·00325 for each 5° C. between 0° and 50°.

Thinking that the hydrocarbon from oil of cedar, for which Walter obtained a vapour-density of 7·5, and to which he assigned the composition $C_{16}H_{26}$, was probably a member of the second group, I prepared some and purified it, as recommended by him, by distillation from anhydrous phosphoric acid. The result was a liquid having the following properties:—

Specific gravity at 18° C. .... 0·9231
Refractive index for A .... 1·4964
Dispersion................................ 0·0276
Boiling point .... 252° C,
Solubility in alcohol .... Slight.

These all agree with the properties of other hydrocarbons of the formula $C_{15}H_{24}$, with which also the proportions of carbon and hydrogen found by Walter are sufficiently in accordance.

Hydrocarbons were also obtained from oil of santal wood and oil of vitivert, by destroying the oxidized constituent by means of sodium; but the yield was small. In each case the oil was sparingly soluble in alcohol and rather viscid. Other properties were as follows :—

	Santal.	Vitivert.
Specific gravity............	0·9190	0·9332
Refractive index for A......	1·4867	1·5061
Boiling point..............	—	255° C.

This is enough to show the analogy to cedrene, but neither specimen was perhaps completely purified.

The general result of these observations, together with those previously made, will be seen by the subjoined table, by which also it will be evident that the middle or fifteen-carbon group is intermediate in all its properties, and that these three groups do not pass by insensible gradations into one another, but are separated by strongly-marked divisions.

	10-Carbon group.	15-Carbon group.	Colophene.
Formula	$C_{10}H_{16}$.	$C_{15}H_{24}$	$C_{20}H_{32}$
Vapour-density	4·7	7·1	—
Character of liquid	Limpid	Viscid	Very viscid.
Specific gravity, at 20° C.	0·846—0·880	0·904—0·927	0·939
Refractive index for A, at 20° C.	1·457—1·467	1·488—1·497	1·5084
Dispersion......................	About 0·027	About 0·029	0·031
Sensitiveness.....................	About 48	About 43	41
Boiling point	160°—176°	249°—260°	315°
Action of sulphuric acid...........	Polymerizes	Doubtful	None.
Solubility in aqueous alcohol........	Freely soluble	Sparingly sol.	Insoluble.
Combination with HCl	$C_{10}H_{16}.2HCl$ and $C_{10}H_{16}.HCl$	$C_{15}H_{24}.2HCl$ and in smaller proportions.	Very small quantity.

There is no difference in specific refractive energy, and the various members of the ten and fifteen-carbon groups at least have powerful

odours, and rotate the plane of polarization strongly, sometimes in one sometimes in the other direction.

OILS CONTAINING OXYGEN.

Many of the essential oils consist, as is well known, of a body containing oxygen, mixed usually with a hydrocarbon of the first or second group. This is sometimes a product of the direct oxidation of the hydrocarbon, and then is generally a feebly acid resin; but in most cases the relation between the two is not apparent. Few of these oils have hitherto been carefully studied. My attention has been confined almost exclusively to those neutral oils which contain only one atom of oxygen.

Citronella.

The oxidised oil of which citronella is principally composed was submitted to analysis. It was purified by repeated fractional distillation till the boiling point was nearly uniform. Combustions were made in the usual manner.

I. Substance boiling at 202°—205° C. Specific gravity at 20° C., 0·8749. 0·4288 grm. gave 1·2230 grm. of carbonic acid, and 0·4215 grm. of water.

II. Substance boiling at 199°—202° C. Specific gravity at 20° C., 0·8741. 0·396 grm. gave 1·1355 grm. of carbonic acid, and 0·386 grm. of water.

These numbers indicate the composition $C_{10}H_{16}O$.

	Experiment.		Calculated.
	I.	II.	
Carbon	77·78	78·19	78·94
Hydrogen	10·92	10·83	10·53
Oxygen (loss)	11·30	10·98	10·50
	100·00	100·00	100·00

This was verified by a determination of the vapour-density.

Difference between weight of air and vapour 0·2912 grm.
Temperature of balance case .... 8° C.
Temperature of sealing .... 254° C.
Capacity of globe .... 110·8 c.c.
Residual air .... 0·6 c.c.
Calculated density of vapour .... 5·83.

The theoretical density should be 5·33, but there was a brown stain left in the globe.

I propose naming this oil citronellol, in accordance with the usual plan of adopting -ol as the termination of the names of bodies of this nature.

The oxygenised oil obtained from wormwood is said also to have the composition $C_{10}H_{16}O$, but its physical properties are very different, as will be seen by the subjoined table, in which I have called it *absinthol*, to distinguish it from the hydrocarbon.

Oil.	Specific gravity at 20° C.	Boiling point.	Refractive Index A, at 20° C.	Dispersion.	Sensitiveness.	Specific refractive energy.	Circular polarisation.*
Citronellol, Penang ..	0·8742	200°	1·4563	0·0251	50	·5219	—
Do. Ceylon ..	0·875	200°	1·4594	0·0262	46	·5251	− 13
Absinthol	0·9267	217°	1·4543	0·0243	43	·4903	+ 134

The refraction equivalent of citronellol is therefore 79·3 or 79·8, instead of the theoretical 73·7, as deduced from the composition $C_{10}H_{16}O$, while the equivalent of absinthol is only 74·5. The discrepancy in the case of citronellol is about the same as is found throughout the great phenyl group, as shown in my paper in the Journal of this Society (year 1870, p. 147), and if the two oils are really isomeric, it suggests an interesting difference in their molecular constitution.

Cajeput.

The oil of cajeput of commerce is said to be obtained from the leaves of *Melaleuca Leucodendron*, but the same oxidised compound was evidently the principal constituent of the oils derived from the leaves of *Melaleuca ericifolia* and *Melaleuca linarifolia*, as well as of *Eucalyptus oleosa*, oils sent to this country from the colony of Victoria.

This compound, though containing oxygen, may be distilled unchanged from metallic sodium. In this way the oils were freed from other oxidised products, and the specimens thus obtained exhibited the following physical properties :—

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* As in the previous paper, the circular polarisation is given as actually measured in a tube ten inches long. It can, of course, be easily reduced to any scale that may be preferred.

Oil.	Specific gravity at 20° C.	Boiling point.	Refractive Index A, at 20° C.	Dispersion.	Sensitiveness.	Circular polarisation.
Cajeput	0·9160	174°	1·4532	·0213	45	— 2 ?
Melaleuca ericifolia	0·8960	173°	1·4560	·0239	48	+ 30
Melaleuca linarifolia....	0·8985	173°	1·4651	·0263	46	+ 11
Eucalyptus oleosa	0·9075	171°—176°	1·4563	·0227	44	+ 10

The composition of cajeputol is well known to be $C_{10}H_{18}O$; the refraction-equivalent of the specimen examined was therefore 76·2, which accords with the theoretical equivalent 76·3.

Carvol and its Isomerides.

In my previous paper it was stated that the oils of spearmint and nutmeg contain oxidised liquids which appear to be isomerides of carvol, the principle which gives its peculiar flavour to the oil of caraway. They were named respectively menthol and myristicol. These have been submitted to a fuller investigation, and it has been found that oil of dill also yields a substance isomeric, or perhaps identical, with ordinary carvol.

There are two ways in which these oxidised oils may be separated,— either by fractional distillation, which must always be an imperfect method, or by taking advantage of the fact that they form crystalline bodies with hydrosulphuric acid, which can be easily purified, and which yield the original oil when decomposed by an alkali. The oil from nutmeg, however, was found not to form such a compound.

The following are the physical properties of the substances above mentioned. Menthol I was prepared by fractional distillation. Menthol II was prepared from the hydrosulphuric compound.

Substance.	Boiling point.	Specific gravity at 20° C.	Refractive Index A, at 20° C.	Dispersion.	Sensitiveness.	Refraction equivalent.	Circular polarisation.
Carvol	227°	0·9530	1·4886	0·0345	46	51·26	+ 145°
Dill carvol	—	0·9562	1·4891	0·0333	45	51·15	+ 108°
Menthol I.	225°	0·9515	1·4839	0·0326	44	50·86	— 103°
Menthol II...........	225°	0·9394	1·4791	0·0311	42	51·00	— 114°
Myristicol	224°	0·9466	1·4848	0·0312	46	51·21	+ 31°

Dill Carvol.—The oxidised oil obtained from dill has the same odour as that from caraway, an odour which can scarcely be confounded

with any other. Like carvol also it forms a crystalline compound when treated with sulphide of ammonium in alcohol. 0·527 grm. of these crystals oxidised by strong nitric acid, and treated with barium salt, gave 0·360 grm. of sulphate of barium.

This result agrees with what should be obtained from the known hydrosulphate of carvole $(C_{10}H_{14}O)_2H_2S$.

	Calculated.	Found.
Carbon.	71·86	—
Hydrogen	8·98	—
Oxygen	9·58	—
Sulphur	9·58	9·37
	100·00	—

I am disposed, therefore, to regard this compound derived from dill as identical rather than isomeric with carvol.

Menthol.—This compound has the very characteristic odour of spearmint, totally different from that of carvol, and it retains the same odour when it has been reproduced from the hydrosulphate.

A combustion was made. 0·3945 grm. yielded 1·159 carbonic acid, and 0·3415 water. This agrees with the formula $C_{10}H_{14}O$.

	Calculated.	Found.
Carbon	80·00	80·10
Hydrogen	9·33	9·62
Oxygen	10·66	—
	100·00	

Two determinations of the vapour-density were made.

Difference between weight of air and vapour..	0·2425	0·2897 grm.
Temperature of balance case	12° C.	12° C.
Temperature of sealing	277° C.	259° C.
Capacity of globe	97·2 c.c.	115·3 c.c.
Residual air..............................	2·6 c.c.	1·3 c.c.
Calculated density of vapour	5·98	5·94

These are both rather above the calculated density, namely, 5·29.

The hydrosulphate forms very readily, giving silky needle-shaped crystals of great beauty. 0·442 grm., oxidised by nitric acid, gave 0·306 of sulphate of barium. 0·2227 grm. oxidised by hydrate of potassium and chlorine gave 0·1605 grm. of sulphate of barium. These determinations give respectively 9·80 and 9·89 per cent. of sulphur, instead of 9·58.

As the composition of these crystals seemed to be the same as that

of the hydrosulphate of carvol, and yet they yield a different oil on treatment with alkali, their relative solubility in ether was examined. At 23° C. one part of the hydrosulphate from the three sources required the following amount of ether to dissolve it:—

From caraway ...... 226 parts.
   ,,   dill .... 279 ,,
   ,,   spearmint .... 216 ,,

Myristicol.—This oil has the characteristic smell of nutmeg, and, unlike the preceding oils, it does not form a crystalline compound with hydrosulphuric acid.

It was found very difficult to purify it by fractional distillation, indeed there was some reason to think that in the process of rectification it was subject to change. An ultimate analysis of portions boiling at somewhere about 220° C. yielded rather too much carbon and hydrogen for the formula $C_{10}H_{14}O$, suggesting the idea of its being still mixed with some amount of a hydrocarbon. The vapour-density was determined.

Difference between weight of air and vapour 0·2512 grm.
Temperature of balance case .... 9° C.
Temperature of sealing.................. 259° C.
Capacity of globe .... 99·8 c.c.
Residual air .... 0·6 c.c.
Calculated density of vapour............ 5·71

This shows at least that myristicol belongs to the C_{10}, and not the C_{15}, or any other group. It accords with theory better than the numbers obtained for menthol do; and the other physical properties resemble those of carvol and menthol so closely that there can be little doubt it is isomeric with them.

Cassia.

The extremely refractive and dispersive properties of Oil of Cassia have long been known to physicists. They depend on a substance that is now recognised as hydride of cinnamyl C_9H_8O. A careful preparation of this was made by the sulphite of sodium process, and it gave the enormous refraction of 1·6045 for A at 11° C. As the specific gravity was 1·059, the refraction-equivalent of the oil was 75·3, being an excess of 17 over the equivalent calculated from its ultimate composition. This excess is greater than that of any other substance known to me, except anthracene, and may, perhaps, throw some light on the molecular constitution of the compound. This interesting question of the refraction equivalents of these hydrocarbons and oxidised

oils has already been referred to in a paper published in our Journal for May, 1870, and I shall probably some day revert to the subject.

Other Oxidised Oils.

In addition to the substances already described, there are several oxidised compounds which have been separated more or less perfectly, and have been examined in regard to their physical properties, though they have not been analysed.

Oxidized oil, from	Specific gravity.	Boiling point.	Refractive Index A.	Dispersion.	Sensitiveness.	Rotation.
Rose	0·881	216°	1·4647	·0283	47	—
Indian geranium	0·884	—	1·4692	·0295	59	− 3
Atherosperma Moschatum.	1·0386	224°	1·5143	·0460	46	+10
Lign aloes	0·8640	200°	1·4601	·0280	—	—

Royal Institution of Great Britain.

WEEKLY EVENING MEETING,

Friday, February 16, 1872,

Sir Henry Holland, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

John Hall Gladstone, Esq. Ph.D. F.R.S. F.C.S. M.R.I.

On the Crystallization of Silver, Gold, and other Metals.

There are few chemical experiments so well known as the growth of the " lead tree," a specimen of which is on the table, together with a " silver tree " that is said to have been made by the late Professor Faraday. These carry our minds back to the time of the alchemists, who called the first " arbor Saturni," and the second " arbor Dianæ;" and they may be looked upon as the types of a large number of phenomena, in which the salt of one metal in solution is decomposed by some other metal. My assistant, Mr. Tribe, and myself have been lately examining these replacements, the metallic crystals which are thus produced, and the forces that act through the liquid.

Our more special attention has been given to the mutual action of copper and nitrate of silver. If these two substances be brought into contact by the intervention of water, there grow upon the red metal what may be well called " trees," and though the analogy between crystals and plants is a very superficial one, yet the resemblances of external form are striking enough, and a nomenclature drawn from the garden seems the most expressive.

It is very beautiful to watch the growth of these silver crystals round a piece of copper under the microscope ; a blue glass underneath adds to the effect, and they are best seen when they reflect a strong light thrown upon them. They may be also thrown upon a screen as opaque objects, but the beauty and lustre of their surface is in this way lost.

The crystals of silver thus produced differ both in colour and form, according to the strength of the solution. If it be very weak— say one per cent.—the copper is fringed with black bushes of the metal, which, in growing, change their colour to white without any alteration of crystalline form that can be detected by a powerful microscope. A stronger solution gives white crystals from the commencement, which frequently assume the appearance of fern-leaves ; while the growth from a still stronger liquid reminds us rather of a

furze bush. If the nitrate of silver amount to 15 per cent., or thereabouts, there occurs a steady advance of brilliantly white moss; and if the solution be saturated, or nearly so, say 40 per cent., this moss is very sturdy, often ending in solid crystalline knobs, or stretching out into the liquid as an arborescent fringe.

In all these cases, however, when the solution in front of the growing crystals has been somewhat exhausted, certain prominent or well-circumstanced crystals seem to monopolize the power, and to push forward through the remaining portions of the liquid. This gives rise to beautiful branches which assume a variety of graceful forms, which it is hopeless to attempt to pourtray by diagrams, but of which the subjoined figures give some of the more characteristic outlines greatly magnified. The weak solutions produce feathery crystals somewhat as in Fig. 1, consisting of a straight central stem
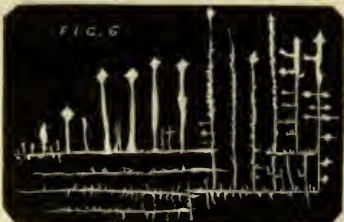
from which grow on either side crystalline rays that terminate in a sharp point, and frequently become themselves the centre stems of a similar crystalline structure. In the outlying growth of a moderately strong solution the apparent regularity of the crystalline form is lost; the main

stem is built up of a confused mass of hexagonal plates, while the side branches are an agglomeration of minute pointed crystals turning in every direction, and producing such jagged outlines as are drawn in Fig. 2. In stronger solutions still the branches lose every appearance of straightness, and they are built up of hexagonal plates so studded with crystalline specks that the whole has the rounded appearance depicted in Fig. 3. The arborescent crystals that succeed the fringes from a saturated solution, are smaller in their foliage than the last, and end in little spherical or botryoidal knobs.

Beside these various forms, there occur all kinds of crystalline combinations, as, for instance, the spray sketched in Fig. 4, where the rough branches have terminated each in a large hexagonal plate, and the flowing past of a weakened solution has afterwards caused the growth of delicate fern-leaves. Often, too, a large expansion will take place in every direction, though joined to the parent stem by an almost invisible thread; or from the point of a long crystal there will branch out to right and left crescent-shaped structures, a process the commencement of which is seen in one of the side rays of Fig. 1. The last traces of silver in the liquid will frequently give rise to delicate crystalline filaments wandering over the surface of the glass, as in Fig. 5.

If a piece of zinc be placed in a solution of neutral terchloride of gold, containing about 9 per cent. of salt, there is an immediate outgrowth of black gold, which speedily changes to an advancing mass of yellow, or perhaps lilac metal in lichen-like forms, from which proceed beautiful fringes of yellow or black, ending generally in such arborescent forms as are represented in Fig. 7. As these branches

Fig. 7.
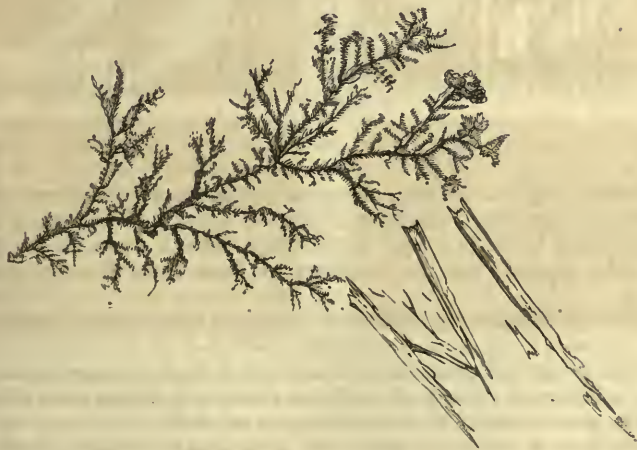
push into the yellow liquid, it becomes colourless even in advance of their points, and it frequently happens that yellow crystals of some salt shoot out in front of the crystallizing metal, which follows them and builds up its advancing fronds at their expense.   This is shown in the figure.   The gold will generally shoot its yellow branches rapidly round the margin of the drop.   Such a running branch has been seen to stop on touching at one point a loose piece of gold, which immediately in its turn became active, and commenced to sprout on its farther side.

Copper salts give round nodules, which have no crystalline appearance when deposited from moderately weak solutions, but a very strong solution of the chloride—about 40 per cent.—yields with zinc first a black thick growth, then arborescent fringes of red metal, terminating in crystals of very appreciable size.

The fringes referred to in the case of these three metals are still more characteristically developed by bismuth.   When a solution of terchloride of bismuth acts on zinc there is an immediate outgrowth of black fringes, such as Fig. 8, where they are seen on an illumi-

Fig. 8.
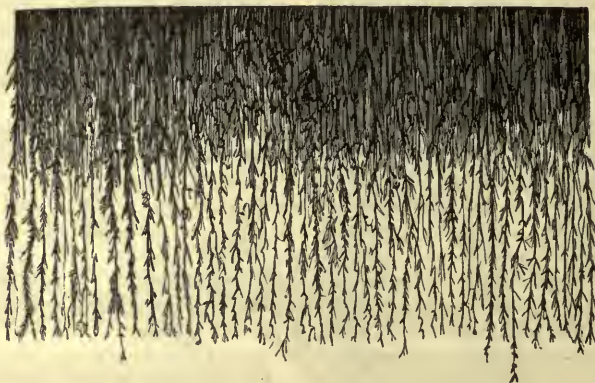
nated field.   These as they advance become more and more arborescent, and as the crystalline character develops itself more they change from black to grey.   Sometimes bismuth presents itself in botryoidal masses, but the tendency to form these fringes is very strong.

Chloride of antimony with zinc also gives these black fringes.

Lead salts yield crystals resembling those of silver ; but leaves of irregular hexagonal plates prevail, and often grow to a large size.

A solution of acetate of thallium, containing 20 per cent. of salt, quickly gives a beautiful forest of thorny crystals.

Sulphate of cadmium gives rise to a small leaf-like growth on

zinc; but a strong solution of the chloride produces an appearance of sticks covered with small spines or knobs.

The new metal indium is thrown down upon zinc in the form of thick white crystals. The deposition is promoted by touching the zinc with a piece of iron.

Tin gives beautiful results. If zinc be placed in a solution of stannous chloride it is quickly surrounded with an outgrowth of prolonged octohedra, and as these advance into the liquid it is easy to observe that the additions of new metal commence at the apex, and that the wave of chemical change proceeds down the lateral edge, occupying some seconds of time in depositing the new layer of material. Frequently, also, there is a luxuriant growth of large flat leaflets, or of symmetrical structures resembling fern-leaves, but with the fronds arranged at right angles, or combinations of these with octohedra, as shown in Fig. 6. These fern-leaves often begin of a dull grey colour; but, as they advance, suddenly change to a brilliant white.

The particular form of these crystalline growths depends, therefore, primarily, on the specific character of the metal; but this is greatly modified by the strength of the solution.

The forms assumed by native metals resemble those produced by this process of substitution. In some cases, indeed, it seems almost certain that the deposition of these minerals was effected in the same way, as, for instance, the silver which occurs sometimes in tufts, sometimes in large crystals, on the native copper of the Lake Superior district. Gold is frequently found in cubes more or less rolled, but the leaf gold from Transylvania bears a striking likeness to the crystals that form in our laboratory experiments. Silver is often found native as twisted hairs or wires of metal—a form that never occurs in the decomposition of its nitrate by copper, but which can be artificially produced in another way.

There has been noticed a singular tendency in old silver ornaments and coins to become crystalline and friable. Here is an ancient fibula from the island of Cyprus, supposed to be at least 1500 years old, which, through the greater portion of its substance, presents a fracture something like that of cast iron, and its specific gravity has been reduced in round numbers from 10 to 9. It contains a little copper. This property of certain metals, or their alloys, to change in condition and in volume, is worthy the attention of those whose duty it is to make our standards. Experiments should be instituted for the purpose of learning what metals or combinations of metals are least subject to this secular change.

These metallic crystals are Nature's first attempt at building. The material is the simplest possible—in fact, what chemists look upon as elementary. But how is the building carried on? What are the tools employed? Where are the bearers of burdens that bring the prepared pieces and lay them together according to the plan of the Great Architect? We must try to imagine what is taking place in

the transparent solution. The silver, of course, existed at first in combination with the nitric element, and for every particle of silver deposited on the growing tree, an equivalent particle of copper is dissolved from the surface of the plate. The nitric element never ceases to be in combination with a metal, but is transferred from the one metal to the other. On the " Polarization Theory," the positive and negative elements of the salt constantly change places and enter into fresh combinations, one consequence of which would be a gradual passage of the nitric element from the growing silver to the copper plate. This actually takes place, and there is a diminution of the salt at the ends of the silver branches, giving rise to an upward current, and a condensation of nitrate of copper against the copper plate, which gives rise to a strong downward current. These two currents are seen in every reaction of this nature. In the case of silver and copper, however, it has been proved that the crowding of the salt towards the copper plate is more rapid than would follow from the usual polarization theory. The instrument employed for determining this point was a divided cell in which two plates, one of silver and the other of copper, connected together by a wire, are immersed each in a solution of its own nitrate, contained in each division of the cell, and separated from one another merely by parchment paper. The crystals of silver deposited on the silver plate in this experiment are very brilliant.

There are other indications of the liquid being put into a special condition by the presence of the two metals which touch one another. Thus zinc alone is incapable of decomposing pure water; but if copper or platinum be deposited on the zinc in such a manner that the water can have free access to the junction of the two metals, a decomposition is effected; oxide of zinc is formed, and hydrogen gas is evolved. At the ordinary temperature the bubbles of gas rise slowly through the liquid, but if the whole be placed in a flask and heated, pure hydrogen is given off in large quantity. We have also found that iron or lead similarly brought into intimate union with a more electro-negative metal, and well washed, will decompose pure water.

As might be expected, the action of magnesium on water may be greatly enhanced by this method; and a pretty and instructive experiment may be made by placing a coil of magnesium in pure water at the ordinary temperature, when there will be scarcely any effect visible, and then adding a solution of sulphate of copper. The magnesium is instantly covered with a growth of the other metal, and at the same time the liquid seems to boil with the rapid evolution of hydrogen bubbles from the decomposed water.

When, however, the force of the two metals in contact has to traverse a layer of water, the resistance offered by the fluid prevents its decomposition. This must also be an important element in the decomposition of a metallic salt dissolved in water, and in fact we have found that the addition of some neutral salt, such as nitrate of potassium, increases the action—apparently by diminishing the resist-

ance of the liquid.   If, too, we increase the quantity of the dissolved metallic salt, we get more than a proportional increase of deposited metal.   Thus, in an experiment made with the different strengths of nitrate of silver on the table, the following results were obtained in ten minutes, all the circumstances being the same except the strength of the solution :—

> 1 per cent. solution dissolved ·025 grm. copper.
> 2   „   „   „   ·078   „
> 4   „   „   „   ·224   „

In fact it has been found that in solutions not exceeding 5 per cent., twice the amount of nitrate of silver dissolved in water gives three times the amount of chemical action; and this is true with other metals also in weak solution.   It may be that this is not the precise expression of a physical law, but it agrees at least very closely with the results of experiment.

The power arising from this action of two metals on a binary liquid may be carried to a distance and produce similar decompositions there.   This is ordinary electrolysis.   Metals have often been crystallized from their solutions in this way, and Mr. Braham has made excellent preparations of crystalline silver, gold, copper, tin, platinum, &c., by using poles of the same metal as that intended to be deposited upon them.   The forms thus obtained are precisely analogous to those produced by the simple immersion of one metal into the soluble salt of another, and illustrate still further the essential unity of the force that originates the two classes of phenomena.

[J. H. G.]

THE

DECOMPOSITION OF WATER BY ZINC

IN CONJUNCTION WITH A MORE NEGATIVE METAL.

BY

J. H. GLADSTONE, Ph.D., F.R.S.,

AND

ALFLED TRIBE, F.C.S.

PURE zinc is incapable of decomposing pure water, even at 100° C., but at a considerably higher temperature it is known to combine with its oxygen. Davy exposed pure water for two days to the action of a pile of silver and zinc plates, separated only by pasteboard, without obtaining any hydrogen; Buff, however, has shown that a very minute trace of gas can be formed at the ordinary temperature by a pair of zinc and platinum plates.

During a series of experiments, of which we have already published an instalment, it occurred to us to ascertain whether by bringing the two metals closer together, and so increasing the electrical tension of the liquid, we could effect the same combination of zinc with oxygen at the ordinary temperature which takes place without the second metal at a very high

temperature. Thin sheets of zinc and copper were hammered together and placed in a bottle filled with distilled water. Small bubbles of gas were formed. The experiment, however, was tried in a more perfect form. Some zinc-foil was allowed to remain in a somewhat dilute solution of copper sulphate until its surface was well covered with spongy copper. The metals were thoroughly washed with distilled water, and then they were immersed in a bottle of distilled water with a delivery-tube. Minute bubbles of gas quickly made their appearance, which proved to be hydrogen, and zinc-oxide was formed. Two experiments were made quantitatively, the gas being collected and measured at the end of 24 or 48 hours. The quantity of gas in cubic centimetres is given in the third and fourth columns of the subjoined Table, corrected for temperature and pressure. The mean temperature in the second column is simply the mean of the maximum and minimum during the period. In experiment A, 33·4 grms. of zinc-foil were employed, being 2·6 metres long and 0·05 wide. The coils were kept apart by muslin. In experiment B there was used 1 metre of similar foil crumpled up.

Day.	Mean temp.	Exper. A.	Exper. B.	Day.	Mean temp.	Exper. A.	Exper. B.
	C.	c. c.	c. c.		C.	c. c.	c. c.
1.	12·8°	117·1	49·6	18.	6·7°	20·0	7·6
2.	12·2	93·8	37·5	19, 20.	6·1	17·2 (×2)	5·7 (×2)
3.	11·7	73·8	27·6	21.	4·4	20·0	6·6
4.	11·1	66·2	24·7	22.	5·0	15·3	4·8
5, 6.	10·0	49·3 (×2)	17·5 (×2)	Interval.			
7.	8·9	41·1	14·9	44.	10·0	20·5	5·5
8.	10·5	40·9	15·8	45, 46.	10·5	22·5 (×2)	6·5 (×2)
9.	10·0	40·9	14·8	47.	11·1	22·3	6·5
10.	7·8	33·8	10·3	48.	11·1	24·1	8·1
11.	6·7	28·0	9·4	49.	11·1	20·5	7·4
12, 13.	6·1	21·9 (×2)	7·7 (×2)	Interval.			
14.	6·1	20·1	7·6	82.	10·0	18·0	4·7
15.	7·2	31·1	10·3	83.	10·0	18·9	6·1
16.	10·0	30·0	10·2	84.	10·0	14·0	5·1
17.	8·3	29·4	8·5				

The two experiments have evidently gone on almost *pari passu* for months, the amount of hydrogen evolved gradually diminishing, but showing, at the same time, a certain dependence on the heat of the day.

Under the microscope the bubbles of gas are seen to form, not on the zinc, but among the copper crystals, and sometimes to make their appearance on the glass at some distance off.

From the position of platinum in the electro-chemical series we anticipated that the effect would be still more marked with that metal in a spongy state on the zinc. It was deposited from the tetrachloride, and, of course, thoroughly washed. There was only 0·6 metre of foil, but the following quantities of hydrogen were obtained :—

Day.	Mean temp.	Vol. in cub. centims.
1.	11·7° C.	143·6
2.	11·4	93·6
3, 4.	10·0	38·8 (×2)
5.	8·6	26·0
6.	10·8	21·0
7.	9·4	17·1
8.	7·7	12·3

The first action, therefore, was about five times as great as in the case of the copper, and it diminished more rapidly, doubtless through the zinc becoming more quickly protected by oxide.

Lest it might be contended that the free oxygen, usually present in distilled water, had been the means of starting this action, the experiment was repeated with water as free from oxygen as could be obtained by boiling. One metre of the same zinc-foil, covered with copper, was employed, and the result was nearly as before, 40 cub. centims. of gas being obtained the first day at the mean temperature of 9° C. This arrangement was taken advantage of to examine the effect of a high temperature. Without removing the delivery-tube, the contents of the flask were heated to near 100° C., when 123·5 cub. centims. of hydrogen were given off in ten minutes. The apparatus was allowed to cool, with the mouth of the tube under water, when the production of gas became small again, and after two days it was again heated nearly to the boiling-point, when it gave off 93·4 cub. centims. in ten minutes; after another period of two days it gave 64·1 cub. centims. and after three days more 132·1 cub. centims. in the first thirty minutes, 108·4 in the second thirty minutes, 94·3 in the third, and 89·9 in the fourth.

Iron and lead, under similar circumstances, also decomposed pure water, and the action of magnesium was greatly increased by conjunction with copper. The effect of the more negative metal was the same as would have been produced by an increase of heat.

In a practical point of view this experiment may serve as a ready means of preparing pure hydrogen; in a theoretical point of view, its interest seems to lie in the fact that the dissociation of a binary compound by means of two metals may take place at infinitesimally short distances, when it would not take place where the layer of liquid is enough to offer resistance to the current, and also in the correlation between this force and heat*.

P.S. March 14.—At the suggestion of Prof. Stokes, we tried to ascertain if the well-known influence of points had much to do with the separation of this hydrogen gas. Two thin plates of copper were taken, the one

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* Since the above was written we have accidentally heard that Dr. W. Russell has been working in the same direction.

smooth, the other rough with electrolytically-deposited copper; these were separated from thin plates of zinc merely by pieces of muslin, and the metals were folded over at each end and hammered together. Each couple was placed in water, and for some days very minute bubbles of gas formed, but only at the junction of the metals, and about equally in each case.

As might be expected, this zinc in conjunction with copper is capable of decomposing other liquids than water. Chloroform yields readily to its power, and iodide of ethyl, which Prof. Frankland decomposed by zinc only at a great heat, is split up rapidly at the ordinary temperature.

ADDRESS

TO THE

CHEMICAL SECTION

OF THE

BRITISH ASSOCIATION.

BRIGHTON, August 14, 1872.

BY

J. H. GLADSTONE, Ph.D., F.R.S.,
PRESIDENT OF THE SECTION.

ONE of my fellow-students in the laboratory of the late Professor Graham began the study of Chemistry because he wanted to be a geologist, and he had read in some Geological Catechism that, in order to be versed in that science, it was necessary, as a preliminary step, to gain a knowledge of Chemistry, Mineralogy, Zoology, Botany, and I know not what besides. My friend became a chemist, and found that enough for the exercise of his faculties. Yet the catechism had truth on its side; for so intertwined are the various branches of observational or experimental research, that a perfect understanding of one can only be obtained through an acquaintance with the whole cycle of knowledge.

Yet, on the other hand, who can survey the whole field even of modern Chemistry? There was a time doubtless, in the recollection of the more venerable of my auditors, when it was not impossible to learn all that chemists had to teach; but now that our "Handbook" has grown so large that it would take a Briareus to carry it, and it requires a small army of abstractors to give the Chemical Society the substance of what is done abroad, we are compelled to become specialists in spite of ourselves. He who studies the general laws of Chemistry may well turn in despair from the ever-growing myriads of transformations among the compounds of carbon. We have agricultural, physiological, and technical chemists; one man builds up new substances, another new formulæ; while some love the rarer metals, and others find their whole soul engrossed by the phenyl compounds.

How is this necessity of specialization to be reconciled with the necessity of general knowledge? By our forming a home for ourselves in some particular region, and becoming intimately conversant with every feature of the locality and their choicest associations, while at the same time we learn the general map of the

country, so as to know the relative position and importance of our favourite resort, and to be able (when we desire it) to make excursions elsewhere.

To facilitate this is one of the great objects of the British Association. The different Sections are like different countries; and, leaving the insular seclusion of our special studies, we can pass from one to the other, and gain the advantages of foreign travel.

From this Chair I must of course regard Chemistry as the centre of the universe, and in speaking of other Sections I must think of them only in their relation to ourselves. There is that rich and ancient country, Section A, which, according to the Annual Report, comprises several provinces, Mathematics, Astronomy, Optics, Heat, Electricity, and Meteorology.

Mathematics and Astronomy.—It was when the idea of exact weights and measures was projected into it that Alchemy was transmuted into Chemistry. As our science has become more refined in its methods its numerical laws have become more and more significant; and it may safely be predicted that the more closely it is allied with general physics, the greater will be the mathematical knowledge demanded of its votary. But till lately the Chemist and the Astronomer seemed far asunder as the heavens and the earth, and none could have foretold that we should now be analyzing the atmospheres of the sun and stars, or throwing light on the chemical composition of planetary nebulæ and the heads of comets. There is in this, too, as in other things, a reciprocal benefit; for we are encouraged to hope that this celestial chemistry will reveal to us elements which have not yet been detected among the constituents of our globe.

Light, Heat, and Electricity.—How intimately are these associated with the chemical force, or rather how easily are these Protean forces transformed into one another! The rays of the sun coming upon our earth are like a chemist entering his laboratory: they start strange decompositions and combinations not only in the vegetable kingdom, but also among inorganic gases and salts; they are absorbed selectively by different bodies which they penetrate, or are refracted, dispersed, and polarized according to the chemical composition and structure of the substance. All this has been the subject recently of much scientific research; and I need scarcely remind you of the beautiful art of photography as one of the results of photo-chemistry, or of the benefits that have arisen from a study of circular polarization, indices of refraction, and especially spectrum-analysis. In regard to the latter, however, I would remark that while the optical examination of the rays emitted by luminous vapours has yielded most brilliant results, there is another kind of spectrum-analysis—that of the rays absorbed by various terrestrial gases, liquids, and solids—which has already borne valuable fruit, and which, as it is far more extensively applicable than the other, may perhaps play a still more important part in the Chemistry of the future. The dispersion of the rays of the spectrum is certainly due to the chemical nature of the body through which they pass; but this is as yet almost unbroken ground waiting for an explorer. As to heat, it has ever been the tool of the chemist; and it would be difficult to overestimate the significance of researches into the specific heat or the melting- and boiling-points of elements and their compounds. The laws of chemical combination have been elucidated lately by thermo-chemical researches; it has been sought to establish a connexion between the absorption or radiation of heat and the complexity of the chemical constitution of the active body; while the power of conducting heat, or of expanding under its influence, offers a promising field of inquiry. As to electrical science, one department of it (Galvanism) is strictly chemical; the electrolytic cell does our work: and indeed we claim half the electric telegraph; for while the needle may oscillate in Section A, the battery belongs to B.

Last in Section A comes Meteorology; and there are chemical questions concerning the constitution of the atmosphere, its changes, and the effect of its occasional constituents upon vegetable and animal life, which merit the deepest attention of the physiologist, philanthropist, and statesman.

If we turn to Section C, there is an outlying province belonging to us—namely, Mineralogy, which lies on the frontiers of Geology. A vast and very promising region is the origin and mode of formation of different minerals: this has attracted some explorers during the past year; but in order to investigate it properly the

geologist and the chemist must travel hand in hand. Geology, in demanding of us the analysis of earths and ores, rocks and precious stones, repays us by bringing to our knowledge many a rare element and strange combination.

When we pass from C to D (that is, from the crust of the globe to the organized beings that inhabit and adorn it) we are introduced into new regions of research. When organic chemistry was young, Cuvier said of it, " Dans cette nouvelle magie, le chimiste n'a presque qu'à vouloir : tout peut se changer en tout; tout peut s'extraire de tout ;" and though we have now learnt much of the laws by which these magical transformations proceed, they far transcend the dreams of the French philosopher ; there is yet no visible limit to the multitude of products to be derived from the vegetable and animal world, and their changes seem to afford boundless scope for chemical ingenuity. The benefit here also is reciprocal ; for the physiologist enters by our aid into the wonderful laboratory of the living plant or animal, and learns to estimate the mode of action of different foods and medicines. There have lately been some good researches of this character. The difficulties are great ; but the results to be achieved are worthy of any effort.

There may be little intercourse between us and the geographers in E ; but we stand in no distant relationship with many of the subjects discussed in F. Economic science embraces the chemical arts, from cookery upwards ; such imperial questions as that of the national standards, or the patent laws, interest us greatly ; the yield of our corn-fields is increased through our knowledge of the constituents of soils and manures ; and upon many of the chemical manufactures depend in no small degree the commerce and the wealth of Britain.

In this most important branch of technical chemistry we need the skill of the mechanician ; and this introduces us to Section G. One of the questions of the day will illustrate the connexion between these varied departments of study. Statistics prove that the consumption of coal is now advancing, not at the gradual pace which recent calculations allowed, but at a rapidly accelerating speed ; and they make the householder anxious about rising prices, and the political economist about the duration of our coal-fields. It is well known that there is a great waste of fuel throughout the country, as the maximum of heat produced by the combustion is very far from being ever utilized ; and it will be for the combined wisdom of the chemist, physicist, and mechanician to devise means for reducing this lavish expenditure, or to indicate other available sources of power.

While this correlation of the natural sciences renders it desirable that the votary of one should have some general acquaintance with the rest, the correlation of all knowledge shows that no education can be complete which ignores the study of nature. A mind fed only on one particular kind of lore, however excellent that kind may be, must fail of proper nourishment. I am not going to say a word against philological studies : I am too fond of them myself for that ; and I could wish that the modern languages were taught more, and the classic languages were taught better, than they are at present. What I do contend for is, that chemistry (or some cognate branch of science) should have an honoured place in the education of every English lady and gentleman. I say purposely " an honoured place ;" for at present where chemistry is introduced we too often find the idea latent which was expressed by one principal of a lady's college, who told a friend of mine that he was to give the girls a course of pretty experiments, but that she did not expect him to teach them any thing ; and we know that when boys repeat chemical experiments at home it is looked upon as an amusement, a philosophical one no doubt, but rather objectionable, inasmuch as they spoil their mother's towels and singe their own eyebrows.

Of course some knowledge of chemistry is indispensable for a large number of our manufacturers, and for the medical profession, while it is extremely valuable to the farmer, the miner, and the engineer. It will also be readily granted that information about the air we breathe, the water we drink, the food we live upon, the fuel we burn, and the various common objects we handle, must be of service to every man. But we are met by the advocates of the old system of education with the remark that the value of school-teaching does not depend so much upon the information given as upon the mental training. This I admit—though it seems to me that if the same training can be secured by two studies, the one of which (like

the making of Latin verses) gives no information at all, and the other (like chemical analysis) imparts some useful knowledge, we should prefer the latter. But I hold that, as a means of educating the mental faculties, chemistry, faithfully taught, has in many respects the advantage over literary studies. There is superabundant scope for the exercise of the memory; the powers of observation are developed by it to a wonderful degree; the reasoning powers may be well disciplined on the philosophy of chemical change, or the application of the laws of Dalton, Mitscherlich, and Avogadro; while the imagination may be cultivated by the attempt to form a conception of the ultimate particles of matter, with their affinities and atomicities, as they act and react upon one another under the control of the physical forces. And I might speak of higher considerations than mere intellectual culture; for surely the works of the Allwise and Bountiful Creator are a more truthful and a purer subject of contemplation for the opening minds of youth, and more in accordance with Christian ideas, than are the crude notions of a past stage of civilization, and the ignorant and gross fancies of a defunct paganism.

There is another requirement in education—the training of the mind to the discovery and recognition of truth. For this purpose philological studies have no fitness; mathematical studies, though peculiarly adapted for it, apply only to cases where demonstrative proof is possible; but the study of physical science is remarkably well fitted for teaching the proper methods of inquiry, and the strict relations between theory and fact. Now the historian, the politician, the mental philosopher, the theologian, or any one else who desires to influence the thoughts of his fellow men, should be in a position to distinguish between truth and error in his own department; and his mind may be well disciplined for this by a study which is less liable to be disturbed by human passions, predilections, or wishes, and where the conclusions are more readily brought to the test of observation or experiment.

Our Government insists on a certain standard of education for all who are allowed to teach in our elementary schools. In those schools which receive no State aid it is only public opinion which can insist that the teacher shall be duly qualified himself. Such bodies as the British Association form this public opinion, and will deserve well of their country if they demand that these masters and mistresses shall know something of the material universe in which they move, and be able to impart to every child such scientific knowledge as shall afford him an interesting subject for thought, give him useful information, and discipline his mental powers.

Among the many services rendered by the monthly reports of the progress of chemistry which the Chemical Society publishes, and the British Association helps to pay for, there is one which is rather salutary than pleasant. They bring prominently before our notice the fact that in the race of original research we are being distanced by foreign chemists. I refer not to the quality of our work, about which opinions will probably differ, but to the quantity, which can be determined by very simple arithmetic. This is a matter of no small importance, not only for the honour of England, but still more for the advancement of science, and the welfare of man. From the Physical Chair of this Association last year, a note of warning was uttered in the following words, after a reference to the sad fate of Newton's successors who allowed mathematical science almost to die out of the country:—"If the successors of Davy and Faraday pause to ponder even on *their* achievements, we shall soon be again in the same state of ignominious inferiority." The President of the Chemical Society also, in the last Anniversary Address, drew attention to the diminished activity of Chemical discovery, and to the lamentable fewness of original papers communicated. He traces this chiefly to "the non-recognition of experimental research by our universities," and suggests that in the granting of science-degrees every candidate should be required, as in Germany, to prove his ability for original investigation.

Concurring in this, I would remark that other causes have also been assigned, and other suggestions have been made. There is the small recognition of original research even by our learned Societies—at least such recognition as will come home to the understanding of the general public. It is true the fellowship of the Royal Society is awarded mainly for original discoveries, and there are two or three medals to be disposed of annually; but these distinctions fall to the lot of the

seniors in science, often men who are beyond the need of encouragement; and though they doubtless are serviceable as incentives, there is many a beginner in the honourable contest of discovery who is too modest even to hope for the blue ribbon of science. While the Victoria Cross is awarded to few, every soldier who has borne part in a victory expects his clasp; and so might every man who has won victories over the secrets of nature, fairly look for some public recognition. It has been suggested, for instance, that the Royal Society, in addition to the F.R.S., might institute an Associateship, with the letters A.R.S., designed exclusively for those younger men who have shown zeal and ability in original research, but whose discoveries have not been sufficient to entitle them already to the Fellowship. It is suggested, too, that the Chemical Society might give some medal, or diploma, or some similar distinction to those who contribute papers of sufficient merit.

But beyond this is the non-recognition of scientific research by society in general. We can scarcely expect the average enlightened Englishman to be any thing but scared by a graphic formula, or a doubly sesquipedalian word containing two or three compound radicals; but he need not continue to talk of the four elements, or of acids being neutralized by sugar. But, indeed, the so-called educated classes in England are not only supremely ignorant of science; they have scarcely yet arrived at the first stage of improvement—the knowledge of their own ignorance. Then, again, there is the excessive preference of practical inventions over theoretical discoveries—or rather, perhaps, the inability to appreciate any thing but tangible results. Thus a new aniline compound is nothing unless it will dye a pretty colour; if we speak of the discovery of a new metal by the spectroscope, they simply ask, What is it useful for? and the rigorous determination of an atomic weight has for them no meaning, or interest, or beauty. The general appreciation of science must be of gradual growth; yet there are wealthy men who know its value, and who might well become the endowers of research. There are, indeed, at present funds available for the purpose—such as the Government Grant, and the surplus funds of this Association; but the money is given simply to cover actual outlay; and this, though very useful, scarcely meets the case of those young philosophers who have no balance at their bankers, and yet must live. Will not some of these wealthy men endow experimental scholarships, or professorships, in connexion with our colleges, institutions, or learned societies? As an instance of the good that may be effected in this way, may be cited the Fullerian professorships; and as a very recent example, worthy of all honour, may be mentioned the purpose of Mr. J. B. Lawes, not only to continue his elaborate experiments at Rothamsted throughout his lifetime, but to place his laboratory and experimental fields in trust, together with £100,000, so that investigations may be continued in the wider and more scientific questions which the progress of agriculture may suggest.

The Government of our country, through the Science and Art Department, renders good assistance to the teaching of science; and if the recommendations of the Royal Commission on Scientific Instruction and the Advancement of Science be adopted, the introduction of practical examinations for the obtaining of certificates for a superior grade of science-master will certainly foster a spirit of research. It has been generally held that the promotion of research is within the legitimate scope of government; and where, as in the case of Aristotle and Alexander, genius and industry have been sustained by princely munificence, the happiest results have ensued. Yet this question of Government aid is a delicate one: for genius, when put into swaddling clothes, is apt to be stifled by them; and were science to depend on political favour or imperial support, it would be a fatal calamity. Still I think it will be everywhere admitted that science might with propriety be subsidized from the public funds in cases where the results may be expected to confer a direct benefit upon the community, and where the inquiry, either from its expense, its tediousness, its uninteresting character, or the amount of cooperation required, is not likely to be carried out by voluntary effort. The astronomical work which is paid for by Government bears upon navigation, and answers both these requirements; and it is easy to conceive of inquiries in our own science that might equally deserve the assistance of the State. Some of these might also more than repay the outlay, though perhaps the profit would not fall into next year's budget.

I believe that this diminution of original research, which we deplore, is partly due to a cause in which we rejoice—the recent extension of science-teaching. The professorships of chemistry are scarcely more numerous now than they were twenty years ago, while the calls upon the professor's time in conducting classes or looking over examination papers have greatly augmented. Thus some of the most capable men have been drawn away from the investigation of nature; and in order to afford them sufficient leisure for the purpose, means must be found to multiply the number of the professorships in our various colleges.

While the rudiments of science are being infused into our primary education, now happily becoming national, while physical science is gradually gaining a footing in our secondary and our large public schools, and while it is winning for itself an honoured place at our universities, it is to be hoped that many new investigators will arise, and that British chemists will not fall behind in the upward march of discovery, but will continue hand in hand with their continental brethren thus to serve their own and future generations.

THE
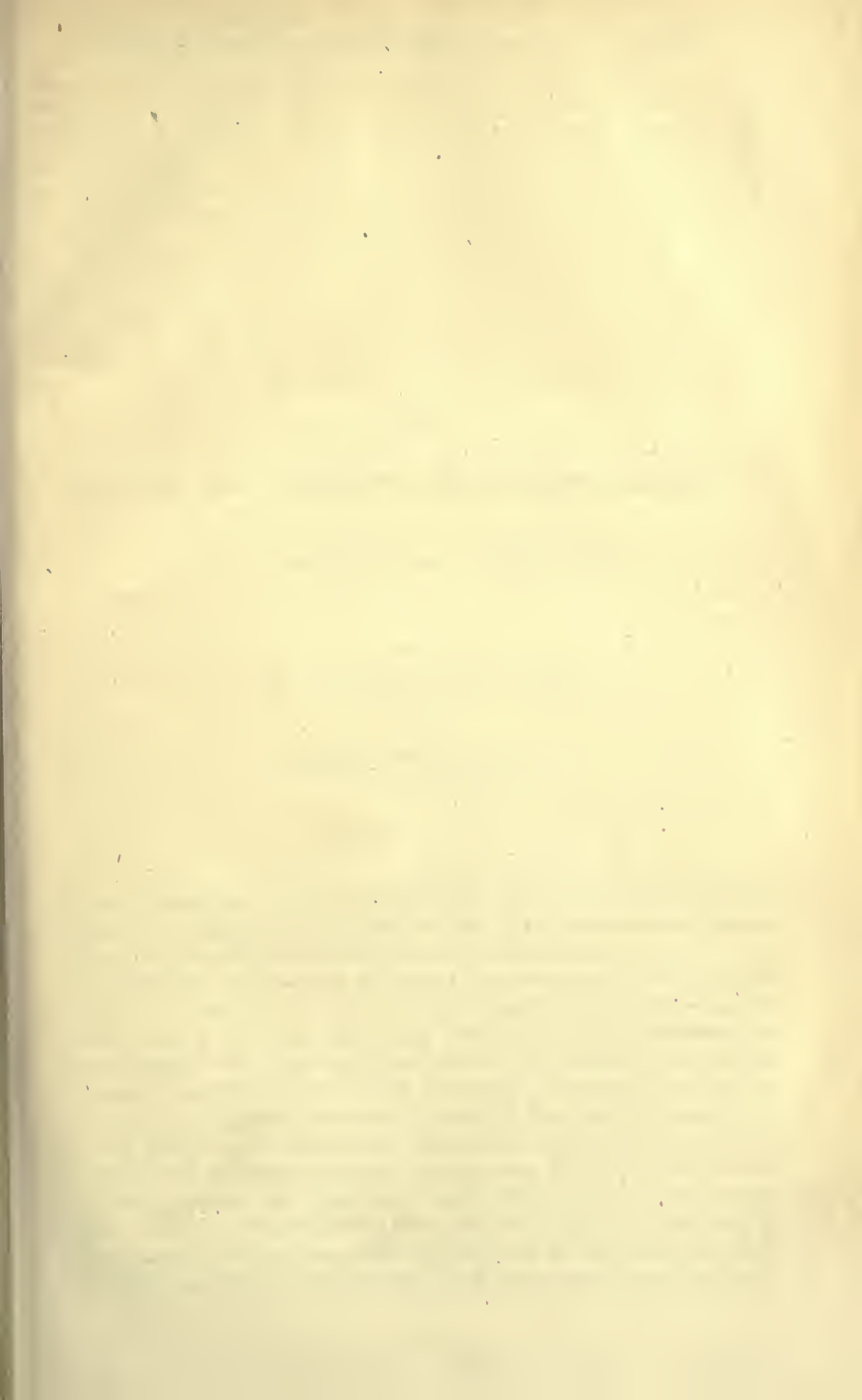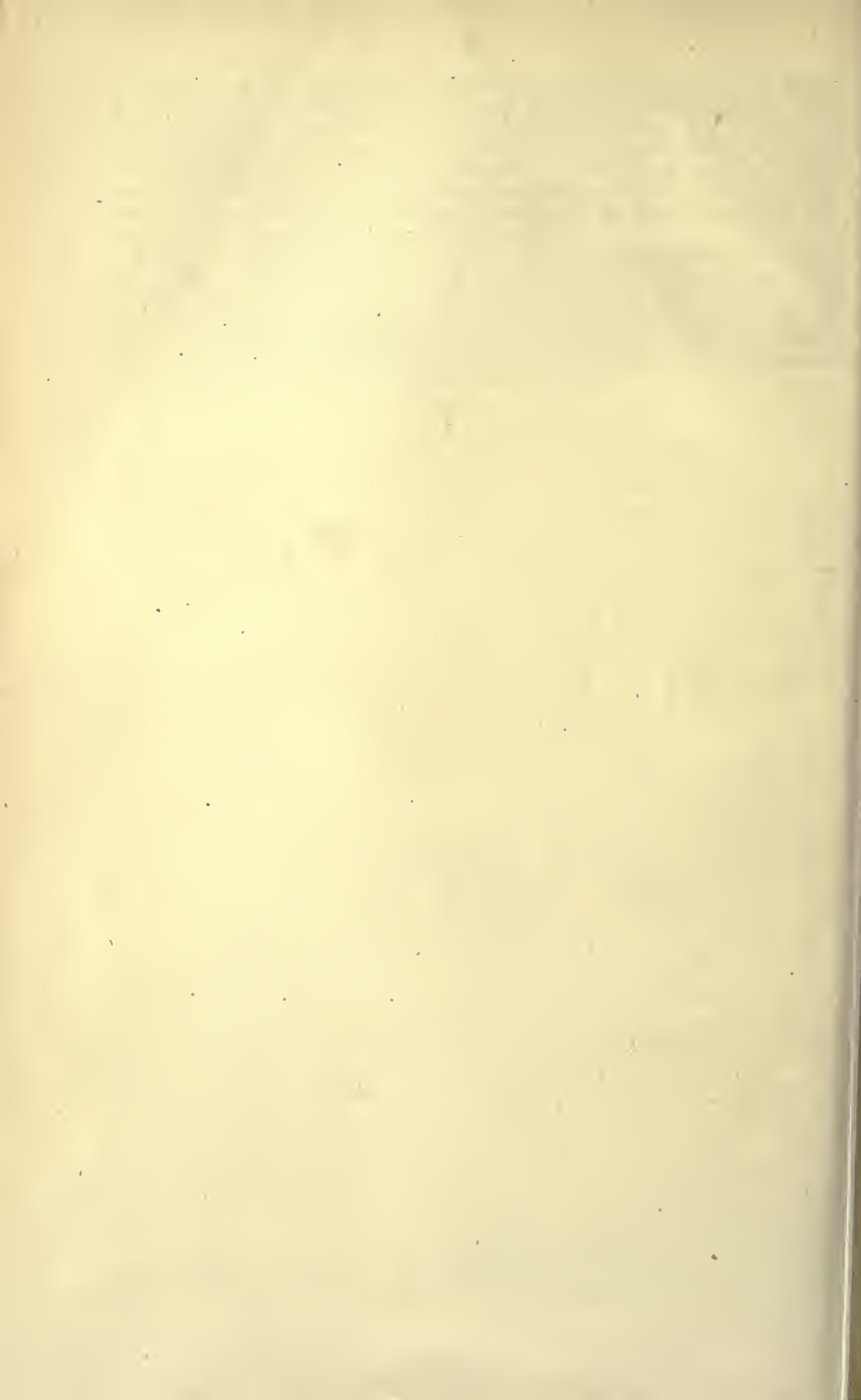
ACTION OF OXYGEN ON COPPER NITRATE

IN A STATE OF TENSION.

BY

J. H. GLADSTONE, Ph.D., F.R.S.,

AND

ALFRED TRIBE, F.C.S.

In our experiments on the action between copper and nitrate of silver in solution, we frequently noticed that the tips of the silver crystals became red, as though coated with a thin layer of metallic copper.

This apparent deposition of a positive on a more negative metal of course raised our curiosity, and led us to look closely into the circumstances under which it occurred. We found that it took place only when the nitrate of silver was exhausted, and only on those silver crystals which remained in metallic connexion with the copper. We found, too, that the cupreous coating formed most readily where air had the freest access, and, in fact, that it would not form at all in vessels from which oxygen was excluded, nor on those white crystals which were far below the surface of the liquid, though they might be in immediate contact with the copper plate. When an inverted jar was filled with nitrate-of-copper solution and silver crystals resting on branches of copper, and the liquid was displaced by oxygen gas, it was found that the tips of the crystals became red, and

the solution gradually filled the jar again by the absorption of the gas. In the same way the oxygen was absorbed from air, or from its mixtures with hydrogen or carbonic anhydride.

This action was further studied by employing plates of the two metals instead of copper covered with silver crystals. When the two plates, connected by a wire, were partially immersed in an ordinary aqueous solution of copper nitrate, it was found that a slight yellowish deposit made its appearance speedily all over the silver plate, and went on increasing for a day or two, while at the air-line there was a thicker deposit, which gradually grew and extended itself a little below the surface. This deposit changed from yellowish to red, and under the microscope presented a distinctly crystalline appearance.

Thinking that this slight crust all over the silver plate was due to air dissolved in the solution itself, we took advantage of the reaction to prepare copper nitrate absolutely free from dissolved oxygen. An ordinary solution of the salt mixed with some silver nitrate was placed in a narrow cylinder, with a long piece of copper-foil arranged somewhat spirally, so as to retain the deposited silver on its surface, and allowed to rest for twenty-four hours. The solution thus obtained was exposed to the action of the conjoined copper and silver plates; but even after some hours there was no dimming of the lustre of the silver plate, except at the air-line, which was sharply defined. The same solution, shaken for some time in the air, produced a yellowish deposit on the white metal in three minutes.

The colour and general appearance of this crust, together with its formation only where oxygen can be absorbed, showed that it was not metallic copper, but the suboxide. This was further proved by the action of dilute sulphuric acid, which resolves it at once into red metallic copper and copper sulphate. There is also another curious reaction, which can only be properly observed under a microscope. When treated with a solution of silver nitrate, this cupreous deposit does not give the ordinary crystals of the white metal; in fact it is only slowly acted upon; but presently there shoot forth thin threads of silver, which run through the liquid, often twisting at sharp angles, while the yellowish crystals change to black. This also was found to be a property of the suboxide of copper.

This deposition of oxide on the silver is accompanied by a corresponding solution of copper from the other plate. Thus, in an experiment made with nitrate-of-copper solution that had been exposed to air, and which was allowed to continue for four days, there was found:—

> Gain of silver plate 0·016 grm.
> Loss of copper plate 0·015 grm.

The copper necessary for the production of 0·016 grm. of suboxide would be a little above 0·014 grm.

The wire connecting the two plates in this experiment is capable of deflecting a galvanometer. The current takes place through the fluid from

copper to silver, that is, in the same direction as if the copper had been dissolved by an acid and hydrogen evolved on the silver plate.

If the two plates have their sides parallel, the suboxide is deposited not merely on that side of the silver plate which faces the copper, but after about a minute on the other side also, showing that in this, as in other cases, the lines of force curve round.

It became interesting to consider what started this electric current. The original observations convinced us that it was not due to the action of oxygen on the copper; but, to make the matter more certain, bright copper and silver plates in conjunction were immersed, the copper in a pure, *i. e.* deoxygenized, solution of nitrate of copper, the silver in an oxygenized solution : the two liquids communicated through the diaphragm of a divided cell. In half an hour the silver plate was covered with a reddish film, while not a trace of tarnish was perceptible on the copper. On continuing this experiment for three hours, it was found that the copper plate lost 0·003 grm., and the silver plate was increased by 0·004 grm. On cleaning the plates, and reversing their position, the copper was covered with a film of oxide, while the silver remained free from cupreous deposit. We believe therefore that, through the simultaneous action of the two metals, the dissolved salt is put into such a state of tension that oxygen brings about a chemical change which otherwise would be impossible, and that this change is initiated in close proximity to the more negative metal.

Though we have examined only this particular reaction, we have satisfied ourselves that it is not an isolated fact. Each of the elements concerned may be replaced by others : thus, the sulphate may be substituted for the nitrate of copper, or platinum may be used instead of silver; chlorine may take the place of oxygen, with the production of the subchloride instead of the suboxide ; and zinc may be employed as the positive metal, with zinc chloride as the salt in solution, in which case copper may be taken as the negative metal, and on its surface will form a deposit of oxide of zinc.

ON AN AIR-BATTERY.

BY

J. H. GLADSTONE, Ph.D., F.R.S.,

AND

ALFRED TRIBE, F.C.S.

THE galvanic battery which we are about to describe is founded on a reaction that we brought under the notice of the Royal Society last spring*. We then showed that if pieces of copper and silver in contact are immersed in a solution of nitrate of copper in the presence of oxygen, a decomposition of the salt ensues, with the formation of cuprous oxide on the silver and a corresponding solution of the copper, while a galvanic current passes through the liquid from copper to silver. We stated, moreover, that this was no isolated phenomenon, but only one of a large class of similar reactions. It seemed desirable to examine more fully the history and the capabilities of the electrical power thus produced.

It was previously ascertained that the combination of the oxygen takes place only in the neighbourhood of the silver; and the following formulæ may serve to render the chemical change and transference more intelligible :—

Before contact,

$$m\mathrm{Ag} + \mathrm{O} + \mathrm{Cu2NO_3} + \mathrm{Cu2NO_3} + n\mathrm{Cu};$$

after contact,

$$m\mathrm{Ag} + \mathrm{Cu_2O} + \mathrm{Cu2NO_3} + \mathrm{Cu2NO_3} + (n-2)\,\mathrm{Cu}.$$
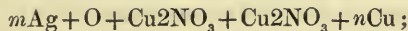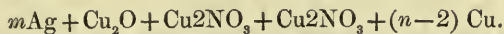
This action is evidently a continuous one until either the oxygen or the copper fails.

Now the oxygen of the atmosphere is practically unlimited in amount, but there is a difficulty in bringing any large quantity of it into contact at once with the silver and the dissolved salt.

To facilitate this, we arrange that the silver plate should have a horizontal position just under the surface of the liquid in the cell; and,

* Proc. Roy. Soc., April 1872, vol. xx. p. 290.

Time after immersion.	In air.	In CO_2.
1 minute.	165	76
5 minutes.	135	62
10 ,,	135	58

As the cell in an atmosphere of carbonic-acid gas showed considerable action, in fact nearly half as much as that in the air, each cell was short circuited for 23 hours, with the expectation that any oxygen in the closed vessel would be used up; and, indeed, the most prominent crystals of silver in the cell in carbonic-acid gas became reddened, while a cuprous deposit extended over the whole of the crystals in the other cell. When, however, the short wires were removed and the galvanometer interposed, the cell in the air gave a deflection of 136, practically the same as before, but that in carbonic-acid gas, instead of showing a great decrease, rose to 80. It was then found that the vessel containing the latter slowly admitted air; so the contents were swept out by a fresh stream of carbonic-acid gas, and it was made properly air-tight. After connexion by a short wire for 3 days the galvanometer indicated a deflection of 20, that of the cell in the air being 110, temperature 10° C. As this showed a very great reduction of the chemical action, carbonic-acid gas was again passed through the vessel for an hour or two; and after a connexion of two more days the indication of the galvanometer was only 3, while the other cell gave 115, the temperature being now 10°·5 C. The action, therefore, was at last reduced almost to nothing; and the original fault in the experiment brought out, perhaps more clearly than would otherwise be seen, how eagerly the solution will absorb even minute quantities of oxygen from the surrounding gas.

An important point to determine was the best strength of the copper nitrate solution. Six per cent. was generally preferred, for two reasons:— first, it gives about the maximum of effect—a solution four times as strong gives less than half the deflection, and a solution only a quarter as strong gives only two thirds; secondly, a stronger solution than this 6 per cent. is apt to produce a deposit, not of pure cuprous oxide, but of a subnitrate, which was supposed to clog up the silver crystals to a greater extent.

Another point investigated was the best proportion between the areas of the metallic surfaces. Experiments were made with vertical plates, in which the silver was kept at a uniform size and the copper was diminished by covering it more and more with varnish; and another set was made in which the copper remained the same, while the silver plate was reduced.

The results may be thus exhibited :—

Proportion of surfaces.		Deflection.		
Silver.	Copper.	Expt. I.	Expt. II.	Expt. III.
1	0·25	24	23	..
1	0·5	28	27	..
1	0·75	31	30	..
1	1·0	33	32	28
1	1·33	..	..	28
1	2·0	..	..	32
1	4·0	..	..	30

The increase of the copper surface, therefore, has comparatively little effect.

Proportion of surfaces.		Deflection.		
Copper.	Silver.	Expt. I.	Expt. II.	Expt. III.
1	0·25	..	..	7·5
1	0·5	..	..	16
1	0·75	..	..	21
1	1·0	33	32	28
1	1·33	41	40	..
1	2·0	56	54	..
1	4·0	96	92	..

The increase, therefore, of the silver or negative metal causes an almost proportionate increase in the chemical action. This, doubtless, arises from the necessity of oxygen, and explains the value of the large surface exposed by the silver crystals in the tray.

The effect of heat on the action of this cell was examined; it increases the action greatly: thus an arrangement which gave a deflection of 40 at 20° C. gave one of 250 at 50° C.; and the augmentation was observed to be much more rapid in the higher than in the lower portions of this range of temperature.

If the formula given above for the reaction be a true one, it follows that every atom of copper deposited on the silver in the state of suboxide must be compensated by an atom of copper dissolved from the copper plate. This was proved quantitatively. In a cell that had been in action for a week the loss of the copper plate was 0·391 grm., while

the suboxide deposited on the silver was found to be equivalent to 0·398 grm. of metallic copper. This deposit of suboxide, though it soon forms apparently a complete covering to the silver, does not greatly diminish the action; it is probably porous, besides being itself a conductor of electricity. In some cases we have found it deposited in crystals sufficiently large to be seen by the naked eye, and which are shown by a magnifying-glass to be regular octahedra.

The internal resistance of this battery, as might be expected, is small.

The electrolytic power of the current was examined. One cell, the plates of which were about two inches in diameter, was found sufficient to decompose such metallic salts as the nitrates of copper, silver, or lead, copper sulphate or stannous chloride, in aqueous solution, when platinum was used for the negative electrode, and for the positive the same metal as existed in the salt experimented on. Six cells were sufficient to decompose dilute sulphuric acid slowly and dilute hydrocloric acid pretty quickly, copper electrodes being employed.

The theoretical interest of this battery lies mainly in the fact that it differs essentially from every other galvanic arrangement, inasmuch as the binary compound in solution is incapable of being decomposed either by the positive metal alone or by the two metals in conjunction; it cannot serve, in fact, as the liquid element of the circuit without the presence of another body ready to combine with one of its constituents when set free.

Grove's gas-battery is essentially different from ours if the oxygen and hydrogen condensed on the platinum plates play the part of the two metals; but it closely resembles ours if hydrogen acts the part of the positive and platinum that of the negative metal; the dilute sulphuric acid, a hydrogen compound, will then be decomposed on account of the simultaneous presence of the oxygen, which can combine with the liberated hydrogen. Viewed in this manner Grove's gas-battery is only a special case of the general reaction which we have described in our previous paper; and the formula will be:—

Before contact,

$$mPt + O + H_2 SO_4 + nH;$$

after contact,

$$mPt + H_2 O + H_2 SO_4 + (n-2)H.$$
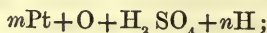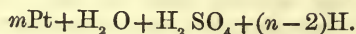
The practical interest of our arrangement lies in the fact that it is an approximation towards a constant air-battery. Should it ever come into use elsewhere than on the lecture-table, it will probably be in the form of a combination of zinc and copper, with an aërated solution of zinc chloride; for that arrangement has an electromotive force six times that of the arrangement we have more particularly studied, and about three quarters that of a Daniell's cell. The numbers representing the difference of potential between the two metals, which were actually

obtained by means of an electrometer belonging to Sir William Thomson, were :—

Silver and copper with deoxygenized copper nitrate   4
Ditto   „   oxygenized   ditto   8 to 11
Copper and zinc with chloride of zinc   62
Ditto   „   water   68
Ditto   „   Daniell's cell   83

Chloride of zinc is preferred to the sulphate, as it offers less internal resistance, and a solution of 20 per cent. is recommended as about the best conductor*. A single cell of this description is capable of decomposing dilute sulphuric or hydrochloric acid, when copper electrodes are employed. The two metals might be arranged as in a Daniell's battery; the zinc would of course require no amalgamation, and the whole might be left for weeks or months without any attention. The oxide of zinc produced generally falls to the bottom of the vessel, and may be separated whenever it is thought desirable.

The power is thus obtained at a minimum of expense, for the oxygen which combines with the zinc costs nothing. Such a battery would appear to be specially adapted to cases where the galvanic current has to be frequently broken, as in telegraphy; for at each period of rest it renews its strength by the absorption or diffusion of more oxygen from the air.

* On the authority of Mr. Herbert MacLeod.

OBSERVATIONS ON THE NATURE OF THE BLACK DEPOSIT IN THE COPPER-ZINC COUPLE.

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.

A QUESTION has been raised as to the nature of the black deposit in the copper-zinc couple that we have lately employed for effecting chemical decompositions, and it has been suggested by Dr. Russell that it contains more or less metallic zinc.

In the present note we give our own observations on the matter; and we are the more glad to do so, as they have a direct bearing on an important point in the history of galvanism.

When a solution of copper sulphate is poured upon zinc, the furry deposit consists of pure copper as long as the solution in contact with the zinc still contains that metal; when, however, the original sulphate has been completely converted into zinc sulphate, other reactions supervene. Through the agency of the oxygen dissolved in the water, a deposit of zinc oxide begins to take place on the copper crystals in the manner described by us in a communication to the Royal Society (*Proc. Roy. Soc.*, 1872, No. 134). The following is the mode of action in the form of an equation, it being understood that the two metals are in contact :—

$$m\mathrm{Cu} + \mathrm{O} + \mathrm{ZnSO_4} + n\mathrm{Zn} = m\mathrm{Cu} + \mathrm{ZnO} + \mathrm{ZnSO_4} + (n-1)\mathrm{Zn}.$$
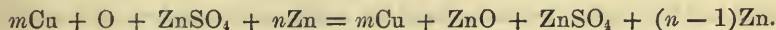
At the same time the decomposition of water, which commences as soon as any copper is deposited on the zinc, goes on continuously with evolution of hydrogen, among the copper crystals. But, in addition to this, there is a formation of metallic zinc, which, if the different substances be allowed to remain in contact, becomes considerable in amount.

A quantitative experiment was made by allowing a couple to remain for rather more than two days in contact with a 1·5 per cent. solution of zinc sulphate, shaking off the black deposit, and treating it with dilute acid. The hydrogen evolved amounted to 5·6 c.c. (corrected), which is equivalent to 0·01625 grm. of zinc, while the copper was estimated at 0·218 grm., showing that the deposit contained 7·4 parts of metallic zinc to 100 parts of copper.

That this metallic zinc is not due to the reduction of the oxide pro-

duced in the manner mentioned above, was proved by its forming equally well in a solution from which the air had been previously expelled by boiling, and to which the atmosphere had no access during the experiment. Such a deposit appears black, or nearly so, to the naked eye; but when examined by the microscope it is seen to consist of branches of crystallised copper, studded with small crystals of metallic zinc. This metallic zinc is, of course, dissolved at once by dilute acids, with evolution of hydrogen, and uncovering of the copper branches; or if it be washed with a solution of cupric sulphate, the zinc is replaced by the more negative metal.

It would appear, therefore, that in the manner in which we have usually prepared our copper-zinc couple, the deposit can contain little or no metallic zinc. If, however, it be allowed to stand some time before it is washed, it will contain zinc, and as this, in the first instance, actually increases the number of points of contact, it may rather increase than diminish the efficiency of the couple.

In the reduction of silver chloride by zinc, we meet with the same phenomena. As long as there is undecomposed silver chloride, the zinc continues to unite simply with the chlorine; but when there is nothing but metallic silver and zinc in contact and surrounded by zinc chloride and water, zinc begins to be deposited on the surface of the silver.

If an aqueous solution of platinic chloride be poured on to zinc, a portion of it is reduced to platinous chloride, as evidenced by the change of colour, while some is reduced at once to the metallic state, forming a grey coating from which bubbles of hydrogen arise, no doubt from the decomposition of water by the conjoined metals. The platinous chloride in solution is reduced in its turn, and the black deposit, after standing awhile in the solution of zinc chloride, was found to effervesce on treatment with acid. In two early experiments made in 1871, before we understood the nature of the action, we found respectively 3·0 and 10·7 per cent. of zinc in the two specimens of the deposit.

Terchloride of gold acts in a similar manner. The deposited gold which had stood in the solution of the transformed chloride was found to contain both zinc oxide and metallic zinc.

The platinum-zinc and the gold-zinc couples decompose water much more rapidly than the copper-zinc couple does, as might be expected from the superior position of the negative metals in the electro-chemical series.

In the early days of the galvanic battery, it was observed that when the sulphuric acid had dissolved a good deal of zinc, a deposit of that metal sometimes occurred upon the copper plates, and it was partly on that very account that Daniell proposed his battery in which sulphate of copper is placed in contact with the copper, and sulphuric acid with

the zinc.   The reaction by which this deterioration of the power occurs
in the old forms of galvanic battery may be thus expressed :—

Before contact—

$$m\text{Cu} \mid \text{ZnSO}_4 \mid \text{ZnSO}_4 \mid \text{H}_2\text{SO}_4 \mid n\text{Zn} ;$$

After contact—

$$m\text{Cu} \mid \text{Zn} \mid \text{ZnSO}_4 \mid \text{H}_2\text{SO}_4 \mid \text{ZnSO}_4 \mid (n-1)\text{Zn}.$$

Now the simple action of the myriads of circuits in our couple is
this—

$$m\text{Cu} \mid \text{H}_2\text{O} \mid n\text{Zn} ;$$

which becomes—

$$m\text{Cu} \mid \text{H}_2 \mid \text{ZnO} \mid (n-1)\text{Zn} ;$$

But where the water contains sulphate of zinc, something like the
following arrangement of molecules must often occur :—

$$m\text{Cu} \mid \text{ZnSO}_4 \mid \text{ZnSO}_4 \mid \text{H}_2\text{O} \mid \text{H}_2\text{O} \mid n\text{Zn} ;$$

and this will become—

$$m\text{Cu} \mid \text{Zn} \mid \text{ZnSO}_4 \mid \text{H}_2\text{SO}_4 \mid \text{H}_2\text{O} \mid \text{ZnO} \mid (n-1)\text{Zn} ;$$
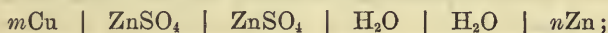
And this is not the end of the deposition of zinc, for the sulphuric
acid thus generated will certainly be swept away by the currents that
are produced at the same time, and may in other places set up the same
reaction that occurs in the old batteries.

The decomposition of the metallic salt in such an arrangement as
Daniell's battery, has sometimes been viewed as the effect of the
nascent hydrogen evolved against the copper or platinum plate.   The
same explanation may be given in this case also, if any prefer it, the
nascent hydrogen being derived, not from an acid but from water.

Whichever be the explanation, it is evident that we have here a con-
tinuous process, by which, eventually, the whole of the zinc will be
oxidised at the expense of the water, but during the process it may not
only crystallise on the copper branches, but be repeatedly removed from
one place to another.

Whether this deposition of zinc has taken place or not before the
couple is washed, matters little to the theory of its action, for
wherever the dissimilar metals meet there is produced an effective
circuit.

In order to determine whether it is perfectly effective when there is
the least transference of zinc, we prepared a couple in the usual way,
except that the sulphate of copper was removed before its blue colour
was destroyed, and with this couple we completely converted 5 c.c. of

ethyl iodide into ethiodide of zinc in twenty minutes, a period shorter than that of the majority of our former experiments.

P.S.—March 20.   As the idea seems to be still entertained by some chemists that the deposit owes its black colour in some way to the presence of zinc, it may not be amiss to state more explicitly our view of the matter.

We fully admit that the black deposit in our couple may usually contain small quantities of metallic zinc: for the sulphate of zinc first formed must be often held within the meshes of the arborescent copper to the exclusion of the copper solution, and thus the secondary action will commence in one place before the primary action is completed in another.   But we cannot assent to the view that the blackness indicates necessarily the presence of zinc: for, among other reasons,—

The first deposit of copper from a very acid solution of sulphate of copper is black.

Some specimens of the black deposit in our couple give much, some a little, and others no perceptible evolution of gas when treated with hydrochloric acid.

Black deposit containing metallic zinc remains black when treated with sulphate of copper.   The copper salt has, of course, destroyed the zinc, as indeed is shown by the deposit no longer effervescing with acid.

Our conviction is that the colour depends mainly on the rapidity of growth of the metallic crystals, and that an arborescent deposit, whether of copper or zinc, if slowly formed, will be black, just as finely divided platinum or gold or silver is black.

RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES.

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.

I. *On Iodide of Ethyl.*

LAST spring we read before the Royal Society a paper in which it was shown that zinc on which copper had been deposited is capable of decomposing water at the ordinary temperature, and at the close of that communication we mentioned that ethyl iodide may easily be decomposed by the same agent (*Proc. Roy. Soc.,* xx, 218).

We propose now to lay before the Chemical Society a description of the reactions of these conjoined metals with this organic body, following the course of the classic memoir of Frankland published in our Quarterly Journal for 1849 (vol. ii, p. 263). The difference between our method and his consists in the fact that while he, using zinc alone, had to confine the ingredients in closed vessels and expose them to a considerable heat, we, using zinc covered with spongy copper, make our experiments with ordinary flasks and delivery-tubes without artificial pressure.

Preliminary Experiments with Zinc.

In order to estimate the value of conjoining copper with zinc in these experiments, it was necessary to make a preliminary trial with zinc alone.

A flask having a capacity of about one ounce (29 c.c.) was filled with zinc foil, about the thickness of writing paper, 14 inches (35 centim.) long and 2 inches (5 centim.) wide, crumpled. To remove any trace of grease this was washed with alcohol, then with ether, and afterwards dried by heating in a current of dry carbonic acid gas.

Five c.c. or 9·5 grams of ethyl iodide were poured into the flask, a long inverted condenser was affixed to it by a perforated cork, and it was placed in a water-bath and heated to the boiling point of the iodide.

This was suffered to continue for an hour, the vapour condensing in the tube and dropping down again upon the metal. On pouring the ethyl iodide into water and shaking it up well, a trace of zinc oxide separated. This existence of a very small amount of action was attributed to those traces of impurity which are always found in zinc.

We repeated the experiment with zinc foil which had been deeply etched by sulphuric acid, since Petal has proposed that the metal in this condition should be used in the production of zinc-ethyl. We

found in the flask a small quantity of a white body soluble in ether, which when poured into water gave 0·04 grm. of zinc oxide. The increase of action was attributed to the etching having brought the impurities of the zinc into greater prominence; but the result was still insignificant in amount.

Action of the Dry Couple on Ethyl Iodide.

An experiment precisely similar to the above in other respects was tried with our couple. The *couple*, for so we shall now designate the zinc with its covering of spongy copper, was prepared by pouring a solution of cupric sulphate containing about 1·5 per cent. of the salt, on to the crumpled zinc foil in the flask, allowing it to deposit the finely divided metallic copper till it loses its blue colour, and repeating this two or three times. We find that a weak solution gives a more effective couple than when a strong one is used. The coating ought to adhere firmly, and present somewhat the appearance of black velvet. The whole must be well washed, first with water, then with alcohol, and lastly with ether, and thoroughly dried by heating it in a current of dry carbonic acid gas.

When ethyl iodide is added to this couple at the ordinary temperature there is little or no sign of action, but upon heating it in the water-bath, some combustible gas is given off, and a large amount of a crystalline body is produced. This has the appearance of Frankland's ethiodide of zinc, and when heated gently by itself, is resolved into zinc-ethyl and zinc iodide.

In order to estimate the amount of zinc-ethyl that may be produced, the following method was employed. The flask was immersed in a bath of boiling water; vapour of ethyl iodide immediately rose in the inverted condenser, but as the liquid fell back it could be seen to diminish, and when this action ceased, the first part of the operation was over. The condenser was then removed, and the flask was fitted with two tubes, one in connection with a carbonic acid generator, and the other bent down so as to dip under a stratum of mercury in a vessel into which water was afterwards poured. Carbonic acid was allowed gently to flow, the white crystalline body was gently heated by a gas flame, and the zinc-ethyl thus produced was swept through the second tube and through the mercury into the water, where, of course, it was decomposed. The oxide of zinc produced was dissolved in dilute hydrochloric acid, precipitated by sodium carbonate and weighed. The results were as follows :—

	C_2H_5I used.	Duration of first operation.	ZnO obtained.	Equivalent to $C_4H_{10}Zn$.
A............	9·5 grams.	15 min.	1·523	2·31
B............	,,	30 ,,	1·346	2·04
C............	,,	45 ,,	1·208	1·83
D............	,,	25 ,,	1·348	2·04
E............	,,	26 ,,	1·728	2·61

The experiments marked A, D, and E, were made at the ordinary pressure, and they afforded the best result both as to yield of zinc-ethyl and quickness of action. The experiments B and C were made at a pressure of from one to two inches of mercury; and in C, where the experiment took the longest time and yielded the lowest result, the amount of gas evolved was found to be 120 c.c. As the greatest possible amount of zinc-ethyl theoretically producible from 9·5 grm. of the iodide is 3·74 grm., it is evident that by our method the bulk of the iodide is converted into ethiodide of zinc, and it is evident also that zinc-ethyl might be prepared in this manner on a large scale.

As it has been recommended to mix ether with the iodide in the preparation of zinc-ethyl, we thought it desirable to see whether it offered any advantage in our mode of operation. An experiment was made as before, except that 5 c.c. of anhydrous ether were added; but though the heat was continued for half an hour, the oxide of zinc obtained was only 0·94 grm., equivalent to 1·43 grm. of zinc-ethyl. The ether therefore appears to retard the action.

Thinking that less gas and therefore more ethiodide would be produced at a lower temperature, we made experiments which showed it was possible to effect the chemical change at 50° C.; but at that temperature it is some time, perhaps half an hour, before the action commences, and it is difficult to know when the whole of the iodide is converted. It is therefore necessary to raise the heat somewhat, especially toward the end of the experiment. In an operation conducted in this manner, with every precaution to ensure the greatest yield, the zinc oxide indicated 2·5 grm. of zinc-ethyl, which barely equals that of experiment E, and is only two-thirds of the quantity theoretically possible. We could not account for the loss of this 33 per cent., unless by supposing that when the crystalline body is heated, other substances are produced besides zinc-ethyl and zinc iodide.

Another experiment was therefore made, in which the usual amounts of substances were heated together in a water-bath, first at 50°, and afterwards to about 85°. The flask was then attached to a delivery-tube passing into a small receiver, from which another tube passed into a vessel of mercury. The apparatus was filled with dry carbonic acid gas, and the crystalline body was gently heated. It became

entirely liquid before the thermometer indicated 75°, and at a higher temperature it rather suddenly gave off the zinc-ethyl, which condensed easily in the first tube and ran down into the receiver, while there passed on a considerable quantity of combustible gas. A portion of this was collected, and after the separation of a little carbonic anhydride, Nordhausen sulphuric acid absorbed nearly half the remainder, leaving a residual gas that burnt with a luminous flame. It was evident therefore that a good deal of the crystalline body suffered a decomposition which yielded gases of two types, probably ethylene and ethyl hydride in equal volumes. A small amount of a bluish black substance was formed in the flask.

Frankland considered that the ethylene and ethyl hydride found among the products of the action of zinc upon the iodide in sealed tubes, are due to the action of ethyl iodide on the ethiodide of zinc; it was thought that by heating our couple with an excess of the iodide, direct evidence of this reaction might be obtained.

3·15 grms. of the couple and 19 grms. of ethyl iodide were therefore heated together for two hours. A few bubbles of gas were given off during the first few minutes. In the flask there remained the spongy copper and a little of the couple unacted on, which were separated from the solution of ethiodide of zinc in ethyl iodide by filtration through asbestos. This liquid was again heated for an hour and a half; only about 10 c.c. of gas were evolved, and that during the earlier part of the time. On heating it in a water-bath, ethyl iodide distilled over; on raising the temperature, the same iodide mixed with zinc-ethyl passed over, and afterwards zinc-ethyl apparently pure. It appears therefore, that whatever may be the case in sealed tubes, ethiodide of zinc is not decomposed by ethyl iodide at a temperature of 70°, and at the ordinary atmospheric pressure.

The question naturally arises, What is the manner in which the couple has acted on the ethyl iodide? The main result is, the crystalline body. This has been viewed in two ways: either as a direct combination of the iodide with the metal $C_2H_5I.Zn$; or as a combination of the zinc-ethyl and zinc iodide $(C_2H_5)_2Zn.ZnI_2$, which are produced by the splitting up of the iodide by means of the metal.

We are inclined to the latter view because, first, the splitting up of a binary compound seems the more especial function of a couple; secondly, there is always found some zinc-ethyl mixed with the crystalline body, even when the temperature has been kept at the lowest; and thirdly, distilled zinc-ethyl will combine with dry zinc iodide, even without the application of heat, giving rise to a crystalline body which resembles in appearance that in the flask, and melts at about the same temperature.

Action of the Couple on Ethyl Iodide and Water.

It was shown by Frankland that if water be present when ethyl-iodide is heated with zinc under pressure, the water also suffers decomposition, and hydride of ethyl is produced in quantity. Now as our couple is able to decompose water at the ordinary temperature, we expected that the reaction just described would take place by means of it without any artificial heat. We were not disappointed.

Five c.c. of ethyl iodide were placed in an ounce flask containing the couple, which had been washed with water, and drained, but not dried. The temperature of the room was only 14°. Evolution of gas took place at once, and it was collected over water in the usual way. About twelve bubbles were given off per minute; then the action slackened, but the rate could be immediately increased by shaking the flask. After 32 hours no more gas was evolved, and the total amounted to 1255 c.c. (corrected for temperature and pressure).

This gas burned with a luminous flame, and was almost wholly soluble in recently boiled alcohol. A portion of it was passed through a set of bulbs containing respectively alcohol and water, and analysed according to Bunsen's method. Nordhausen sulphuric acid caused no diminution of volume.

After removal to the eudiometer the following were the data obtained :—

	Observed vol.	Tempera-ture.	Difference of Hg level.	Baro-meter.	Vol. at 0°C. and 1 m.
Gas used (moist)	18	16·0°	455	755·14	6·58
After adding air and O (moist)	283	16·8°	188	755·47	152·66
After combustion (moist)	262	16·2°	209	755·92	136·86
After absorption of CO₂ (dry)	236	9·3°	235·2	759·2	124·07

giving the following results as compared with those calculated for hydride of ethyl.

	Found.	C_2H_6.
Gas burnt	6·58	—
Contraction	15·8	16·45
Carbonic anhydride	12·79	13·16

This, taken in conjunction with its physical properties, confirms the belief that this gas was hydride of ethyl, but mixed probably with a small amount of free hydrogen arising from the action of the couple on the water alone.

The 1255 c.c. of gas collected, making allowance for loss by the

carrying over of iodide vapour, and absorption by water, fairly represents the total amount which could be obtained theoretically, viz., 1365 c.c.

The residue in the flask had a faint odour, suggesting that of acetic ether. There was a white substance adhering to the undestroyed couple. On distillation some water passed over with a trace of an ethereal body, but no iodide of ethyl. From what was left, alcohol dissolved out zinc iodide, leaving the hydrate.

Action of the Couple on Ethyl Iodide and Alcohol.

The substitution of alcohol for water in the above reaction makes little change, though the couple was found to have no effect whatever upon absolute alcohol itself, even at a boiling temperature. The evolution of gas commences at a few minutes after the substances have been placed together, if the temperature be 20°; but if it be lower, a quarter or half an hour is required to start the action; but when it is once fairly started, the temperature rises, and the decomposition proceeds rapidly.

In one experiment 5 c.c. of ethyl iodide were poured on to the couple which had been washed with alcohol but not dried. The action was moderated by immersing the flask in water, at about 19°. The amount of gas obtained was, after correction, 1170·7 c.c.

In another experiment 5 c.c. of ethyl iodide were mixed with 10 c.c. of absolute alcohol, and poured upon the dry couple. The action was allowed to take its natural course, and in 15 minutes after it had begun, 1060 c.c. of gas were collected. The whole evolved amounted to 1114 c.c.

On repeating the latter experiment, using 5 c.c. of alcohol, the gas collected was 1101 c.c.

It would appear therefore that the yield of gas is not quite equal to what is obtained by the agency of water instead of alcohol, and of course it does not approach so nearly the theoretical amount of 1365 c.c.

The gas had the same properties as before, and was analysed in the same way. Sulphuric acid did not alter its volume, at least not beyond the extent of possible errors of observation.

Two combustions were made.

	Volume observed.	Tempera-ture.	Difference of Hg level.	Baro-meter.	Vol. at 0° C. and 1 m.
			mm.		
I. Gas used (moist)....	21	17·1	449	758·95	7·882
After adding air and O (moist) ..	293	16·6	173·5	757·39	162·25
After combustion (moist)	269	17·1	198·5	756·64	142·51
After absorption of CO_2 (dry)......	244	17·1	223·5	756·38	126·87
II. Gas used (moist)....	16·5	16·6	453·0	758·1	6·239
After adding air and O (moist) ..	261·3	16·6	205·9	758·1	137·17
After combustion (moist)	240·5	16·6	226·5	758·1	121·55
After absorption of CO_2 (dry)	217·8	17·7	250·2	762·5	109·19

These numbers give the following results :—

	I.		II.	
	Found.	Calculated.	Found.	Calculated.
Gas employed	7·88	—	6·24	—
Contraction	19·74	19·70	15·62	15·60
Carbonic anhydride......	15·64	15·76	12·3	12·48

It appears therefore that the gas is pure ethyl hydride.

In Frankland's experiment, where the substance had been exposed to a high temperature and to pressure, he had reason to believe that the residue contained oxyiodide of zinc and ether. We could never detect the least odour of this latter substance either in the flask or in the bulbs through which the gas had bubbled. The residue in our case was a substance of a gummy consistency, in which some beautiful prismatic crystals were once observed; it dissolves completely in absolute alcohol, and from this alcoholic extract water throws down a bulky precipitate of zinc hydrate. A certain measure of this alcoholic solution gave on analysis 0·694 grm. of silver iodide, and 0·230 grm. of zinc oxide, of which 0·104 grm. was precipitable by water.

This indicates the proportion in atomic weights :—

Zinc.................... 1·0
Iodine .... 1·04
Zinc removed by water.... 0·45

On distilling off the alcohol in a water-bath, a yellowish liquid remained, which when heated to about 205°, gave off more alcohol,

leaving a dark yellow solid.   This when heated over a gas flame, blackened and was resolved into a combustible gas, a small quantity of a liquid having the smell of ether, and a residue from which alcohol extracted zinc iodide, leaving zinc oxide and some carbon.

The original substance is probably an iodo-ethylate of zinc.   The original reaction would appear therefore to have been—

$$C_2H_5I + C_2H_6O + Zn = C_2H_6 + \left.\begin{matrix} C_2H_5O \\ I \end{matrix}\right\} Zn,$$
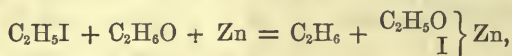
which is perfectly analogous to what has before been supposed to take place in the reaction with water.

$$C_2H_5I + H_2O + Zn = C_2H_6 + \left.\begin{matrix} HO \\ I \end{matrix}\right\} Zn.$$
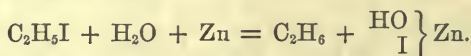
From this paper it will be gathered that the copper-zinc couple supplies the means of preparing both zinc-ethyl and ethyl hydride on a large scale with perfect ease.   Of course the zinc foil may be replaced by granulated zinc.   The rapidity and simplicity of the action renders it well suited for lecture illustration.

In another paper we hope very shortly to describe its action on the homologues of ethyl iodide.

RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES.

Part II. *On the Iodides of Amyl and Methyl.*

By J. H. GLADSTONE, PhD., F.R.S., and ALFRED TRIBE, F.C.S.

FRANKLAND found that " iodide of amyl is acted upon by zinc with much more difficulty than the corresponding ethyl compound;"[*] he speaks of the necessity of " a very nice management of the temperature," and though he mentions zinc-amyl among the results of the reaction, he never obtained it in any quantity by this method. For the decomposition of iodide of amyl he resorted to the use of zinc-amalgam in powder in sealed tubes at a temperature a little above that of the boiling-point of the liquid. He thus obtained, not zinc-amyl but a mixture of three hydrocarbons, viz., amyl, $C_{10}H_{22}$, a light liquid boiling at 155°; hydride of amyl, C_5H_{12}, an exceedingly mobile liquid with an agreeable odour, boiling at 30°; amylene, C_5H_{10}, another limpid liquid boiling at 35°, and combining with fuming sulphuric acid.

It appeared to us therefore a point of special interest to ascertain whether our copper-zinc couple was capable of effecting the decomposition of amyl iodide with production of an organo-metallic body.

On performing the experiment in a manner analogous to that described in our previous communication on iodide of ethyl, we at once perceived that it was a question of temperature. At 100° there is no appreciable action, but upon heating the flask somewhat higher in a paraffin bath, decomposition ensues. It however, proceeds slowly, unless the temperature be raised to near the boiling-point of the iodide (146°); but at such a temperature 5 c.c. of amyl iodide are completely converted in about a quarter of an hour. Volatile bodies are formed which, if allowed to distil over into a receiver, are found to have the properties of amyl hydride and amylene described above, while in the flask there remain another limpid liquid and a white crystalline body, which appears to be but sparingly soluble in it. If the flask be now heated a little higher, this liquid distils over, and on examination proves to consist almost wholly of one

[*] Chem. Soc. J., iii, 31.

substance, having the properties of Frankland's amyl. At about the temperature necessary to distil off the amyl, there begins to form a body which fumes in the air ; and at 160°, or above, the white crystals suffer decomposition, with production of a liquid that distils over, and leaves a solid substance in the flask. The liquid is again almost pure amyl.

As both stages of this reaction have yielded amyl, this would appear to be a productive method of preparing that substance. It was evidently worthless, however, for the preparation of zinc-amyl, unless it could be modified in some favourable direction. Such a modification was not far to seek. If during the formation of the crystalline body, the volatile hydrocarbons are caused to fall back again into the flask, and then the contents are rapidly distilled off either over a flame or by a bath at 160° or higher, a good deal of zinc-amyl is carried over with the other liquids, and collects with them in the receiver.

The following are the quantitative experiments that were performed; arranged according to the temperature at which the first operation was conducted. As in the case of the ethyl iodide 5 c.c. were always employed, and the amount of zinc compound distilled was estimated by shaking the contents of the receiver with water, and weighing the oxide produced.

Experi-ment.	Temperature of bath.	Duration of heating.	Amount of decomposition.	ZnO obtained.	Zinc-amyl indicated.
A	100°	1 hour	none	none	— grm.
B	127°—131°	1 ,,	about 2 c.c.	0·095 grm.	·244 ,,
C	127°—130°	3 hours	complete	0·324 ,,	·834 ,,
D	138°—142°	2 ,,	,,	0·222 ,,	·571 ,,
E	140°—160°	2 ,,	,,	0·150 ,,	·386 ,,
F	145°	7·5 min.	4·25 c.c.	0·320 ,,	·824 ,,
G	145°	15 ,,	complete	0·444 ,,	1·143 ,,
H	145°	20 ,,	,,	0·406 ,,	1·045 ,,
I	177°—188°	1 hour	,,	none	— ,,

As the amount of zinc-amyl theoretically attainable from 5 c.c. of the iodide is 3·97, the best of the above experiments gave only ·28 per cent. of what might have been hoped for.

It then occurred to us that if the zinc-amyl, which is said to boil at 220°, could be raised in vapour at or near the temperature at which the crystalline body splits up, that is about 150°, it might be procured in larger quantity. The first part of the operation was therefore performed as before, namely, by heating the flask in a paraffin bath at 145° for 15 or 18 minutes, but a pump was attached to the distilling apparatus, and a good vacuum was made. The flask was then heated, and the vapour was pumped into water.

The results were :—

Experiment.	Second heating.	ZnO obtained.	Zinc-amyl indicated.
J	By gas flame........	0·621	1·59
K	By paraffin bath	0·678	1·73

This shows a much larger yield of the zinc-amyl, in fact 40 and 43·5 per cent. of the theoretical quantity.

Of course in the receiver it is mixed with the hydrocarbons, especially the less volatile amyl. By careful heating, the great bulk of that liquid may be separated by distillation; but as we operated on small quantities and the zinc-compound is easily decomposed, we never obtained it in the pure state; still, it answered sufficiently to the description given by Frankland of the zinc-amyl he prepared by the action of mercuric-amyl on zinc, to leave no doubt that it was the same substance.

Frankland has pointed out the perfect analogy of the decomposition of amyl iodide into the liquid $C_{10}H_{22}$, C_5H_{12}, and C_5H_{10}, with the secondary reactions by which ethyl iodide yields the gaseous C_4H_{10}, C_2H_6 and C_2H_4. But working as he was obliged to do, with zinc-amalgam at a temperature above the boiling-point of amyl-iodide, he obtained little else than the secondary action which we find to accompany the formation of amyl-iodide of zinc through the agency of the couple at a lower temperature. We may extend the analogy, for just as the crystalline $C_2H_5I.Zn$ forms in the one case, so does the crystalline $C_5H_{11}I.Zn$ form in the other; two molecules of the one split up by heat into $C_4H_{10}Zn$ and ZnI_2, and two molecules of the other into $C_{10}H_{22}Zn$ and ZnI_2, while in each instance this splitting up is accompanied by a similar secondary reaction. In the case of the ethyl compound, however, this secondary reaction appears to be principally—

$$2C_2H_5IZn = ZnI_2 + Zn + C_2H_6 + C_2H_4.$$
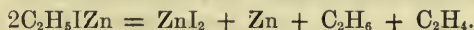
while in the case of the higher carbon molecule, it is mainly—

$$2C_5H_{11}IZn = ZnI_2 + Zn + C_{10}H_{22}.$$
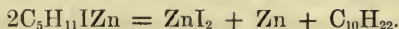
Action on Amyl Iodide and Water or Alcohol.

As zinc alone is capable of decomposing a mixture of amyl iodide and water at 140° with production of amyl hydride, it was interesting to ascertain whether our couple would do the same at a lower temperature.

The experiment was conducted as in the case of the ethyl-compound by

pouring 5 c.c. of the iodide on to a couple washed with water but not dried. Action was found to take place slowly at the temperature of the laboratory 10°, but in a water-bath at 100° it proceeded so rapidly that it appeared complete in an hour and a-half. The vapours produced were made to pass up a tube about 16 inches long, which condensed any volatilised water or iodide, and then through a Liebig's condenser into an iced receiver. A liquid was thus collected which was lighter than water, not miscible with it, and boiled when the vessel containing it was immersed in a bath at 33°, a thermometer in its vapour registering 29°. Any further proof that this was the same hydrocarbon as Frankland obtained at a higher temperature, seemed unnecessary. The residue in the flask resembled that from the ethyl compound treated in the same manner.

We repeated this experiment, using absolute alcohol instead of water, and found as before that the action proceeded slowly at 10°, but at 70° it seemed to be complete in three-quarters of an hour. The same volatile hydrocarbon was produced, and the residue in the flask gave the properties of the iodo-ethylate of zinc described in our former paper as occurring when ethyl iodide and alcohol react in presence of the couple.

This circumstance, and the fact that no permanent gas is given off during the experiment with the amyl compound, show that it is the radical of the iodide, and not that of the alcohol, which is hydrogenised.

This reaction offers a ready method of preparing pure amyl hydride.

Action on Methyl Iodide and Water or Alcohol.

Methyl iodide was found to be decomposed very slowly by a dry copper-zinc couple, even at the boiling-point of the liquid.

If, however, the couple be wet with water, decomposition proceeds even at the ordinary temperature. An experiment made as usual with 5 c.c. of the iodide at 12°, the flask being shaken from time to time, evolved permanent gas during 18 hours, at the end of which time 1414 c.c. had been evolved.

This gas, after being washed, burned with a blue scarcely luminous flame. It was passed through bulbs containing alcohol to remove any vapour of the iodide, and afterwards through water, and analysed by Bunsen's method. There was no absorption by fuming sulphuric acid.

After removal to the eudiometer, the following data were obtained :

	Vol. observed.	Temp.	Diff. of Hg. level.	Baro-meter.	Vol. at 0° C. and 1 m. pressure.
Gas used (moist)	35·944	10·2	451	745·72	10·027
After addition of air and O (moist) .... }	246·369	10·3	249·5	751·56	117·210
After combustion (moist)....	217·27	9·0	277·9	750·3	97·339
After absorption of CO_2 (dry)	198·86	11·0	297·1	752·31	87·238

which gave the following numbers as compared with those calculated for methyl hydride :—

	Found.	Calculated.
Gas burnt	10·03	—
Contraction	19·87	20·06
Carbonic acid ..	10·10	10·03

The amount of this gas which might have been evolved, according to theory, from 5 c.c. of methyl iodide is 1782 c.c.

The residue in the flask was similar to that in the corresponding reaction with iodide of ethyl and water. The nature of the reaction is evidently the same, and may be thus expressed—

$$CH_3I + H_2O + Zn = CH_4 + Zn \begin{cases} I \\ HO. \end{cases}$$
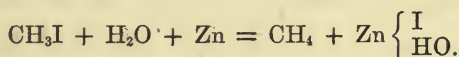
When 10 c.c. of absolute alcohol were added to 5 c.c. of methyl iodide, and the mixture was submitted to the action of the couple at 10°, it was about 20 minutes before evolution of gas commenced, but then the temperature inside the flask rose, and the action proceeded so rapidly that in half an hour 500 c.c. were obtained. The total collected was 897 c.c. In another experiment, where the iodide was poured on to a couple wet with alcohol, and the flask was immersed in water at 12°, the gas amounted to 1063 c.c. It burnt with a blue scarcely luminous flame. The residue in the flask gave the reaction of the iodo-ethylate of zinc, as in the analogous experiments with ethyl and amyl-compounds.

Either of the reactions just described offers a simple method for preparing pure methyl hydride, or marsh-gas.

RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES.

Part III. *On Normal and Iso-Propyl Iodides.*

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.C.S.

As the iodides of ethyl and of amyl are decomposed by our copper-zinc couple at a temperature below their respective boiling points, we anticipated that the same would be the case with the intermediate iodides of propyl and butyl. As these bodies offer to us isomeric modifications, an additional point of interest was included in their investigation.

In the present paper we confine ourselves to the propyl compounds, but hope at some future time to describe the reactions with all the butyl iodides, if we are fortunate enough to procure specimens of them.

Action of the Dry Couple on Isopropyl Iodide.

The isopropyl compound, being the more accessible body, was the first examined. Our specimen had a constant boiling point, and seemed perfectly pure.

If it be heated to 50° with a dry copper-zinc couple a faint cloud appears in the flask after the lapse of some minutes, and gases are evolved. The action proceeds rapidly, and no further change takes place even at a boiling temperature.

In one experiment 5 c.c. (8·73 grms.) showed signs of action in fifteen minutes, and during the next four minutes 453 c.c. of gas were collected and the action ceased, leaving in the flask a body liquid at the ordinary temperature and a solid (probably iodide of zinc) which it held mainly in solution. When air was admitted to the flask white fumes formed in the neighbourhood of the liquid. When this was gently heated over a gas flame 424 c.c. of gas were quickly evolved and a small quantity of a liquid distilled. This liquid fumed in the air, and on decomposition by water gave 0·068 zinc oxide, which would be equivalent to 0·127 grm. of zinc-propyl.

In another experiment with the same quantity of isopropyl iodide at 50° the action commenced in twelve minutes, lasted six minutes, and yielded 425 c.c. of gas. The flask was then heated to 100° and kept at that temperature for twenty minutes, but no gas was evolved. It was then raised   132° and maintained at 132°—138° for two hours.

During the whole of this time gas was slowly evolved, amounting to 283·2 c.c., while a little liquid distilled. The temperature was then increased, and 81·6 c.c. of gas and a further trace of liquid were obtained. The total gas collected was therefore 789·8 c.c. The amount of zinc-oxide formed by the decomposition of the two small portions of liquid in the tubes and receivers was ·018. The amount of liquid in the receiver was certainly more than ·033 grm., leading us to the belief that a little dipropyl (C_6H_{14}) is formed, as there was no iodide.

As in the course of our experiments on amylic iodide (p. 678 of this volume) we found more zinc-amyl produced when the contents of the flask were heated *in vacuo*, we adopted the same plan in this instance also.

Another preparation was made at 50° and it was then heated to 132° while the gas was constantly being pumped out. A good deal was given off, but also a much larger quantity of the liquid body than in the previous experiments. On the admission of air to the receiver this liquid was suddenly changed into a light brown solid, with evolution of much heat. On addition of water it was decomposed with a crackling noise. The oxide of zinc was ·544, which, if the liquid were zinc-propyl, would indicate 1·01 grm. of that body prepared from 8·7 grms. of the iodide.

The gas given off during the reaction at 50° was analysed by Bunsen's method, after it had been passed through a set of bulbs containing respectively alcohol and water. When it was treated with Nordhausen sulphuric acid the following data were obtained from two different preparations :—

	Volume observed.	Tempera-ture.	Difference of Hg. level.	Baro-meter.	Vol. at 0° C. and 1 m.
I. Gas used (dry)	65·57	18·2	95	750·06	40·51
After treatment (dry)..	34·85	13·5	101·8	758·19	22·11
II. Gas used (dry)	165·1	8·8	98	756·66	118·14
After treatment (dry)..	95·7	9·3	82·8	756·66	62·69

It appears therefore that the gas capable of being absorbed was per 100 volumes—

Expt. I.	Expt. II.	Mean.
45·43 vols.	44·55 vols.	44·99 vols.

A portion of the gas not absorbed by sulphuric acid was exploded in the usual way, and the following are the results :—

	Volume observed.	Tempera- ture.	Difference of Hg. level.	Baro- meter.	Vol. at 0° C. and 1 m.
I. Gas used (moist)	27·15	14	422	763·78	8·68
After adding air and O (moist)	284·39	14	165·8	763·78	158·83
After combustion (moist)	251·47	14·5	199	763·78	132·19
After absorption of CO₂ (dry)	213·14	16·7	220·5	749·81	106·57

This gives the following results, which are compared with those calculated for hydride of propyl:—

	Found.	C_3H_8.
Gas burnt	8·68	—
Contraction	26·64	26·04
Carbonic anhydride	25·62	26·04

Another combustion gave nearly the calculated amount of carbonic anhydride, but the first contraction exceeded still more what was expected. The interior of the eudiometer, however, after the explosion presented an appearance which led us to think that some combination of oxygen with nitrogen had taken place. This of course would account for an excess of contraction.

Some of the gas which had not been treated with sulphuric acid was burnt.

	Volume observed.	Tempera- ture.	Difference of Hg. level.	Baro- meter.	Vol. at 0° C. and 1 m.
Gas used (moist)	22·57	11	416·2	746·76	7·11
After adding air and O (moist)	284·49	10	157·7	746·51	159·36
After combustion (moist)..	258·82	9·2	180·8	745·1	139·61
After absorption of CO₂ (dry)	225·04	9·3	217	756·66	117·67

Now if we assume that 100 volumes of this gas contain 45 volumes of propylene, as we are warranted to do by previous experiments, the 7·11 vols. may be supposed to be made up of 3·2 vols. of propylene, C_3H_6, and 3·91 vols. of hydride of propyl, C_3H_8. Calculating from this, we obtain numbers very similar to those found—

	Found.	Calculated.
Gas employed	7·11	—
Contraction	19·75	19·73
Carbonic anhydride	21·94	21·33

It may therefore be concluded that the gas evolved at 50° is a mixture consisting of nearly equal volumes of C_3H_6 and C_3H_8.

The gas evolved in the second part of the operation was also examined. The amount collected when the contents of the flask were submitted to dry distillation was rather less, as already shown, than that collected during the reaction at 50°, and when treated with Nordhausen sulphuric acid it was found to contain about half its volume of an olefine. It would appear therefore that the gas given off in the two parts of the reaction is of essentially the same composition, and the probable reaction is as follows:—

$$\left\{ \begin{array}{l} Zn + 2C_3H_7I = ZnI_2 + C_3H_6 + C_3H_8 \\ 2Zn + 2C_3H_7I = ZnI_2 + Zn(C_3H_7)_2. \end{array} \right.$$
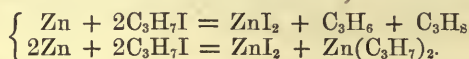
The two reactions go on simultaneously in about equal proportions at 50°.

$$Zn(C_3H_7)_2 \text{ heated to } 132° = Zn + C_3H_6 + C_3H_8.$$

Action of the Couple on Isopropyl Iodide and Water.

It was found that this iodide, like those previously examined, is decomposed at the ordinary temperature by the couple wet with water. The action commences at once.

In the first experiment with 5 c.c. of the iodide, gas was slowly evolved for 48 hours, the temperature varying from 7° to 11°. The amount collected was 820 c.c.

In another experiment, where the temperature was 13°—16°, 831 c.c. were collected in 40 hours.

The gas thus produced was found to be readily soluble in alcohol and to burn with a luminous flame. Two portions treated with Nordhausen sulphuric acid gave an absorption amounting respectively to 7·93 and 9·73 per cent.

After removal of the residuary gas of one of these portions to the endiometer the following data were obtained:—

	Volume observed.	Temperature.	Difference of Hg. level.	Barometer.	Vol. at 0° and 1 m.
Gas used (moist)	27·85	12	413	773·43	9·5
After adding air and O (moist)	416·6	6·2	28	754·07	293·3
After combustion (moist)..	388·3	6·2	50·6	754·38	264·65
After absorption of CO_2 (dry)	368·6	9	74·6	735·84	236·28

which gives the following results, agreeing very closely with those calculated for propyl hydride:—

	Found.	C_3H_8.
Gas used	9·5	—
Contraction	28·65	28·5
Carbonic anhydride	28·37	28·5

Action of the Couple on Isopropyl Iodide and Alcohol.

The action of this iodide with alcohol was more rapid than with water, as was also the case with the iodides previously examined.

5 c.c. mixed with 10 c.c. of absolute alcohol were poured upon the dry couple, at a temperature of 9°. In four minutes there was an evolution of gas, which proceeded so rapidly that the flask had to be immersed in cold water, at 7°. Nevertheless in four more minutes the action was complete, and 823 c.c. of gas had been collected. In another experiment 5 c.c. of the iodide were poured upon a couple which had been washed with absolute alcohol, but not dried. The temperature was 17°. Evolution of gas commenced in two minutes, when the flask was at once immersed in water at 13°. In ten minutes, 885 c.c. had been collected. The whole gas evolved in this experiment was 913 c.c.

If the propyl contained in 5 c.c. of the iodide were wholly converted into C_3H_8, it should yield 1150 c.c. of gas. The actual yield, therefore, whether in the case of water or alcohol, is considerably less than the theoretical, but this probably arises from its solubility in the water over which it was collected, and the carrying over of some vapour of the iodide.

Action of Zinc alone.

As isopropyl iodide is so easily decomposed by the copper-zinc couple, it occurred to us that it might be attacked by zinc alone. On trying the experiment with clean zinc foil it was found that no action whatever took place at 50°, though the heat was continued for an hour, but that on immersing the flask in boiling water, evolution of gas commenced in eight minutes, and proceeded so rapidly, that in twelve minutes more it was complete, and 605 c.c. of gas had been collected. The residue in the flask fumed slightly in the air, and when heated gently over a flame, it gave off 177 c.c. of gas, and a small quantity of the volatile zinc compound decomposible by water.

For the purpose of comparison, a flask containing 5 c.c. of the iodide, and the ordinary copper zinc couple was similarly immersed in boiling water. Evolution of gas commenced at once, and in five minutes the action was complete, 490 c.c. of gas being collected.

This illustrates the fact that even when zinc alone is capable of effecting a decomposition, the copper-zinc does it at a lower temperature, or with greater rapidity; also that the decomposition is not

identical in the two cases, for the more elevated temperature causes a larger proportion of the organic compound to be resolved into hydride and olefine.

On repeating the above experiment with pure zinc, finely granulated, we found that with it also the reaction took place at the boiling temperature.*

The reaction with isopropyl iodide and water and clean zinc takes place exceedingly slowly at 20°; when the usual quantities were employed, only 35 c.c. of gas were collected in 24 hours. When the temperature is raised, the production of gas is greatly increased.

The reaction with the iodide and alcohol with clean zinc foil at 20°, commenced in a few minutes, and the action proceeded rapidly, but not so violently as with the couple. With pure zinc granulated, we obtained the same result.

Propyl hydride has been prepared by Schorlemmer (*Proc. Roy. Soc.*, 1869, p. 373) by the mutual action of isopropyl iodide, zinc, hydrochloric acid and water, but the reaction with zinc alone in presence of alcohol, seems to offer a better method of preparing this gas; better, in fact, than when the couple is employed, as it is more manageable.

Action of the Dry Couple on Normal Propyl Iodide.

We procured a specimen of the normal propyl iodide, which boiled almost constantly at 101°, and we found that it was attacked very slowly by clean zinc foil, or pure zinc, even at its boiling point, and that it was acted on by the couple very differently from the iso-compound.

In the first place 5 c.c. (8·81 grms.) were heated in contact with the dry couple for an hour at 50°, the temperature at which the iso-compound is attacked, but no action whatever took place. A similar portion was afterwards heated with the couple, at 80°, in the manner described in a previous paper (*Chem. Soc. Journal*, May, 1873, p. 445). In forty minutes dense white fumes were observed in the flask, but they were not accompanied by any appreciable evolution of gas. The heating was continued for twenty minutes, when the flask was allowed to cool, and its contents were washed out with ether. When water was added to this solution, a brisk effervescence ensued, and hydrated oxide of zinc was thrown down. The amount of zinc-oxide was 1·414, which would be equivalent to 2·636 grms. of zinc-propyl, and that would be 67·4 per cent. of the amount theoretically obtainable from 5 c.c. of the iodide.

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* This reaction is the more remarkable, as Schorlemmer finds that isopropyl iodide is not decomposed by sodium, even at the boiling-point. See *Proc. Roy. Soc.*, 1867, p. 34.

In a subsequent experiment the same quantity of iodide was heated in contact with the dry couple, by means of a chloride of calcium bath at 109°. At the end of ten minutes the return flow of the liquid appeared to have ceased, while very little gas—not more than 50 c.c.— had been evolved. When cool, the organic compound in the flask did not crystallise, but seemed, as in the case of the iso-compound, to be a liquid body, holding a solid in solution. It was distilled in a current of carbonic gas, in the same way as the ethyl compound had been distilled, and a liquid came over, which, when decomposed by water, yielded 1·32 gram of ZnO, equivalent to 2·46 grams of zinc-propyl, or 62·9 per cent. of the possible amount. Yet the distillate contained some undecomposed propyl iodide.

The experiment was repeated with this difference, that after the return flow had ceased, which required nine minutes, the flask was exposed for another nine minutes to the heat of a bath at 117°. The product was liquid, as before, but the distillate contained no iodide, and yielded 1·578 ZnO, equivalent to 2·94 grams of zinc-propyl, or 75·2 per cent. of the possible quantity—a larger yield than we ever obtained in the case of zinc-ethyl.

A third experiment was made with a specimen of the normal propyl iodide obtained from another source. The result was as before; but the liquid product was distilled into a weighed receiver, previously filled with carbonic acid, and was found to weigh 2·712 grams, or 69·3 per cent. of the theoretical amount of zinc-propyl, obtainable from 5 c.c. of iodide employed. On re-distillation, the great bulk came over between 146° and 148°.

A preparation was then made on a larger scale, 15 c.c. of the iodide were taken, and three times the usual amount of couple, a two-ounce flask being still employed.* When it was heated in a bath at 109°, the return flow ceased in thirteen minutes, but a temperature of 117° was maintained for twenty minutes more, in order to insure complete conversion. There was some gas evolved during the whole period, but the production diminished considerably towards the end. The quantity collected was 290 c.c. When the bath was heated at 149° distillation commenced, but it was finished off at 182°. The flask then contained some reduced zinc, partly in a crystalline form. The liquid in the receiver weighed 8·563 grams, or 73 per cent. of the possible amount of zinc-propyl. On re-distillation in a bath, the whole passed over between 142°—148°, leaving a small residue of metallic zinc.

Zinc-propyl thus produced is probably the same body as that which Cahours obtained by double decomposition, though that chemist has

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* Two-thirds of the couple was transferred from another flask in which it had been prepared, dried, and annealed.

not yet published a description of it. Our compound is a colourless mobile and volatile liquid, of specific gravity 1·098 at 15° C., and boiling at about 146°. When exposed to the air it takes fire spontaneously,* burning with a bluish white flame. If dry air be allowed gradual access to it, it is converted into a white solid, which does not fume in contact with air, but is decomposed by water, with a crackling noise and effervescence.

1·0885 grm. of the liquid yielded on decomposition with water, 0·583 grm. ZnO, giving the following percentages :—

	Found.	Calculated for $Zn \begin{Bmatrix} C_3H_7 \\ C_3H_7 \end{Bmatrix}$.
Zinc.........	42·98	43·04

Action of the Couple on Normal Propyl Iodide and Water, or Alcohol.

When 5 c.c. of the normal iodide were poured upon the couple wet with water at 13°, gas was almost immediately evolved, but the action proceeded very slowly. In about 84 hours it ceased, when 884 c.c. were found in the receiver. The temperature had varied from 13° to 19°. This gas was not diminished in volume by treatment with Nordhausen sulphuric acid ; it dissolved readily in alcohol, and burnt with a very luminous flame.

When 5 c.c. of the normal iodide were poured upon the couple wet with absolute alcohol at 15°, evolution of gas commenced in twenty minutes, soon after which the temperature of the flask rose considerably. The action was complete in 45 minutes, when 766 c.c. had been collected, but some iodide had distilled over unchanged.

In another similar experiment the action commenced in 28 minutes, when the flask was at once immersed in water at 17°. Gas was evolved for about 24 hours, when 868 c.c. had been collected.

The amount of gas, as usual, falls short of the quantity possible on the supposition that the propyl passes over entirely as the hydride, C_3H_8, viz., 1161 c. c., but it shows at least that the gas obtained corresponded to 2 volumes.

Comparison of Results.

This inquiry has added to the evidence already existing of the comparative instability of the iso-propyl compounds. We have noticed the following points of contrast :—

The iso-propyl iodide is rapidly decomposed by zinc alone at its boiling point, 89°, while the normal propyl iodide is decomposed very slowly by zinc alone at its higher boiling point 101°.

* It was found that zinc-propyl was rendered not spontaneously inflammable by admixture with a little less than 3 per cent. of propyl iodide.

The iso-compound is decomposed by the copper-zinc couple at about 50°; the normal compound at about 80°.

In this decomposition about half of the iso-compound is split up into permanent gases; little, if any, of the normal compound is so split up.

The resulting liquid in the one case (zinc-isopropyl?) is scarcely volatile; that in the other case (zinc-propyl) rises easily in vapour, notwithstanding its high boiling point. The first is decomposed at about 132°, giving mainly gases and metallic zinc: the second distils over unchanged at a higher temperature.

The reaction between the propyl iodide and water, or alcohol, with the couple, takes place much more rapidly in the case of the iso-compound than in that of the normal compound; while an olefine makes its appearance during the decomposition of the first, but not of the second.

On comparing these results with those previously obtained with the ethyl and amyl compounds, it is evident that it is the normal, and not the iso-propyliodide that is acted upon in an analogous manner. The main difference perhaps is that there seems to be no crystalline propyliodide of zinc, but that the reaction is mainly, if not wholly—

$$2C_3H_7I + 2Zn = ZnI_2 + Zn(C_3H_7)_2.$$
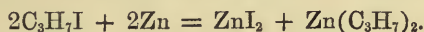
Additional Notes on the Couple.

In performing these experiments with 5 c.c. of liquid, we have employed zinc foil having a surface of about 260 square centimeters on each side and weighing about 9 grams. It is crumpled up and torn to pieces just so as to introduce it into the flask, and leave irregular spaces between the different pieces. After treatment with copper sulphate, the zinc sulphate produced should be thoroughly washed away; and particular attention should, of course, be paid to the purity of the alcohol and ether with which it is dried, for any deposit on the surface would be highly injurious. In drying the couple in a stream of carbonic acid it has been found convenient to heat it till the zinc begins to soften, not melt; on cooling, the zinc will be found to be annealed, and may be gently pressed to the bottom of the flask.

It has been suggested to us that zinc foil necessarily contains some quantity of lead, and that this may have an important bearing on the reaction. Specimens of zinc from various sources have, therefore, been examined, and have given the following percentages of lead:—

Zinc foil used for couple* ....   0·96 and 0·93 per cent.
Granulated zinc, commonly used in our laboratory.............................   1·13 per cent.

* Supplied by Messrs. Hopkin and Williams.

> Granulated zinc from Dr. Frank-
>   land's laboratory ....   0·96 per cent.
> Ordinary sheet zinc ....   0·89   „

It appears, therefore, that the zinc foil contains no more lead than the form of zinc which has been usually employed, and we have no evidence to show whether the presence of one per cent. of this metal is favourable or unfavourable to the action of the couple.

A comparative experiment was made with 18 grams of granulated zinc on which copper had been deposited in the same manner as before. It gave with normal propyl iodide the same reaction as the couple made of foil, but much more slowly. This superiority of the foil depends doubtless on its presenting so large an extent of surface in a given cubical space, and therefore forming so large a number of small circuits between the two metals and the liquid.

RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES. PART IV. ON IODIDE OF ALLYL.

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.C.S.

After investigating the action of our copper-zinc couple on the iodides of propyl, we turned aside from the series containing the C_nH_{2n+1} radicals, in order to examine its action on the corresponding member of the series which contains the C_nH_{2n-1} radicals.

Action of the Dry Couple on Allyl Iodide.

On pouring the liquid iodide of allyl upon the metallic couple, there is a sensible rise of temperature, but the action, whatever it may be, stops quickly, unless extraneous heat be applied. At 100° the decomposition is moderately rapid, little or no gas is evolved, and the only organic products appear to be a liquid which has the properties of di-allyl, and a non-volatile resin, apparently isomeric with allylene.

In one experiment a flask containing 5 c.c. (9 grams) of the iodide, with the usual amount of the copper-zinc couple (see *Journ. Chem. Soc.*, 1873, p. 969) was heated in a bath of boiling water for two hours. During this time there distilled over a slightly coloured liquid, which weighed 2·6 grams. On re-distilling this liquid, the first portion that came over, about one-third of the whole, was colourless, mobile, lighter than water, and capable of combining with sulphuric acid to form a brown, treacly mass. The remaining two-thirds consisted principally of undecomposed allyl iodide. Neither of these portions contained a trace of zinc. The flask was then heated to 200° for half-an-hour, but no further allyl iodide, or any other volatile body, was driven off, and the residue was treated with water. This dissolved out the iodide of zinc, but left a resinous body, which was insoluble in alcohol, but readily soluble in ether. Its ethereal solution, on evaporation, gave a brownish substance, which, when dried at 100°, weighed 0·31 grm. An ultimate analysis was made of 0·2060 grm., which yielded 0·6805 CO_2 and 0·181 H_2O. This indicates it to be a hydrocarbon, and probably of the composition $n(C_3H_4)$, the slight excess of carbon being probably due to some carbonization having taken

place during the drying of the body, as was rendered the more likely
by its somewhat brown colour.

	Calculated, C_3H_4.	Found.
Carbon........	90·00	90·10
Hydrogen.......	10·00	9·76
	100·00	99·86

The iodide of zinc formed in this experiment was determined, and it
showed that 6·8 grams of the iodide had been decomposed; and the
quantities of the two organic products lead to the conclusion that the
major part was split up by the action of the couple into iodide of zinc
and diallyl, thus:—

$$2(C_3H_5I) + Zn = ZnI_2 + \begin{cases} C_3H_5 \\ C_3H_5. \end{cases}$$
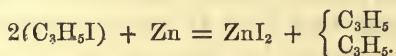
while about a fifth part was in some way deprived of hydrogen, but
instead of forming gaseous allylene, C_3H_4, it formed apparently an
isomeric or polymeric modification. If this C_3H_4 were due to the
splitting up of diallyl, $\begin{cases} C_3H_5 \\ C_3H_5 \end{cases}$, its complementary hydrocarbon would
of course be produced, as in the case of the C_nH_{2n+1} series; but this
was never the case, and we are disposed to attribute the reduction
to oxide of zinc unavoidably present in the couple, especially as a trace
of water was always observed during the reaction.

Unwilling to relinquish the hope of obtaining zinc-allyl, we tried
the action of the couple on the iodide in presence of ether. A decom-
position was found to take place at the ordinary temperature, and to
proceed rapidly. In one experiment, where 9 grams of the iodide were
mixed with twice its volume of pure ether at 12°, the temperature
immediately rose; the flask was immersed in water at 12° for 15 minutes,
and on removing it, the temperature again rose, but in 10 minutes it
had cooled. Little or no gas was evolved, and the products of the
reaction were entirely in solution. An estimation of the iodine in
combination with zinc showed that 8·43 grams of the iodide, or nearly
the whole quantity, had been decomposed. Now if the reaction under
these circumstances were simply $2C_3H_5I + Zn = ZnI_2 + \begin{cases} C_3H_5 \\ C_3H_5 \end{cases}$, the
atomic ratio of the iodine to the zinc in the solution would be 1 : 0·5;
but if a reaction should take place similar to that which occurs with
the monad positive radicals of the alcohol series, viz., $C_3H_5I + Zn = ZnC_3H_5I$, then it is evident that the atomic ratio of the iodine to the
zinc would be 1 : 1. In the experiment detailed above the ratio was
found to be 1 : 0·587. Thinking that this excess of zinc might arise
from the presence of some alcohol or water in the ether employed,

though it had been distilled three times from sodium, a portion of the same ether was boiled with sodium for $2\frac{1}{2}$ hours, and then carefully distilled from the same metal. To obviate any injurious rise of temperature on mixing the materials, the flask was kept immersed in water at 11°, and it was suffered to remain untouched for two hours. The reaction was complete. The ethereal solution, on shaking with water, gave a precipitate of zinc oxide, and the ratio of the iodine and zinc was found to be 1 : 0·584, the same as in the previous experiment. On another trial, in which the temperature was kept still lower, and the decomposition not allowed to proceed to completion, the ratio was found to be 1 : 0·600.

This excess of zinc can scarcely therefore be attributed to the presence of any alcohol or water in the ether employed. Moreover, had it been so, there would have been found, as will be presently shown, about 120 c.c. of propylene. No gas, however, was evolved. Yet this is inconclusive, for ether itself is capable of dissolving propylene, indeed we found it to dissolve 12·8 times its volume at 13°, and therefore the gas would scarcely make its appearance as such. But this objection is susceptible of an answer, for a mixture of alcohol and water, just capable of dissolving the ether, separates about half the gas from solution, and no effervescence was observed when the ethereal solution was thus diluted.

This excess of ratio, and the separation of oxide of zinc on the addition of water, are, after all, inconclusive grounds for assuming that some allyl-iodide of zinc is produced; and our attempts to get any indication of free zinc allyl completely failed. No fuming was ever seen, and we could separate from the ethereal solution, no organic compound, except the liquid having the properties of diallyl and the non-volatile hydrocarbon before described.

Zinc alone acts very slowly on allyl iodide in presence of ether.

Action of the Couple on Allyl Iodide and Water.

Pure granulated zinc was found to have no effect on allyl iodide in presence of water, at the ordinary temperature. Our usual zinc-foil had a little action, and the copper-zinc couple a great deal; thus in two comparative experiments, continued for 24 hours, 32 c.c. of gas were evolved by means of the former, 550 c.c. by the latter.

5 c.c. (9 grams) of the iodide were added to the ordinary quantity of the couple wet with water. There was an immediate evolution of gas, which continued for 48 hours, when 918 c.c. had been collected. The temperature was about 17°. The gas burnt with a very bright flame, dissolved readily in absolute alcohol, combined with bromine, and fuming sulphuric acid absorbed 99 per cent. of it. It needs no further proof that the hydrogenation of the C_3H_5 had not proceeded

so far as to produce either dipropyl, $\left\{ \begin{array}{l} C_3H_7 \\ C_3H_7, \end{array} \right.$ or propyl hydride, C_3H_8; but had stopped at the first stage, giving rise to the olefine, C_3H_6, propylene.

The reaction would appear to be—

$$C_3H_5I + H_2O + Zn = ZnI.HO + C_3H_6,$$
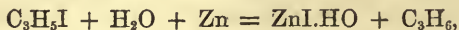
and the theoretical amount of gas producible from 9 grams would be 1200 c.c.

Action of Zinc on Allyl Iodide and Alcohol.

The couple acts so violently on iodide of allyl when mixed with alcohol, that our experiments were confined to the action of zinc alone, and even this becomes unmanageable, unless means are employed for keeping down the temperature.

5 c.c. of the iodide, with 10 c.c. of absolute alcohol, were added to 10 grams of pure granulated zinc. Evolution of gas commenced immediately. The flask was at once immersed in water at 14°, and the action ceased in six minutes, by far the greater portion of the gas having been produced in the first two minutes. The gas, collected as usual over water, measured 1035 c.c.

Alcohol of spec. grav. 0·805, was found to act more slowly, on account of the retarding influence of the water, and when it is more dilute, the water interferes with the completion of the reaction, through the formation of a crust of compact oxide on the zinc, most probably from the decomposition of the iodo-ethylate of zinc produced. (See *Journ. Chem. Soc.*, May, 1873.)

A very convenient method for preparing pure propylene is to place some granulated zinc in a flask provided with a delivery tube and thistle-funnel, cover the zinc with absolute alcohol, and add iodide of allyl, as the gas is required.* Some gas prepared in this manner was purified by passing through aqueous alcohol and water successively. It burnt with a smoky flame, combined with bromine, to form an oily body boiling pretty constantly at 143°, and dissolved rapidly and completely in absolute alcohol and fuming sulphuric acid. The sole reaction, therefore, with alcohol would appear to be

$$C_3H_5I + C_2H_6O + Zn = Zn \left\{ \begin{array}{l} C_2H_5O \\ I \end{array} \right. + C_3H_6.$$
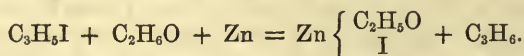
* The nearest approach to this method is that of Tollens and Heiniger, only they employ hydrochloric acid in addition, which gives impure gas.

RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES. PART V. ON THE BROMIDES OF THE OLEFINES.

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.

PARALLEL with the series of haloïd combinations of such radicals as ethyl, propyl, and amyl, is the series of haloïd combinations of the olefines. Thinking it would be interesting to examine the action of our copper-zinc couple on them, we had specimens of the bromides of ethylene, propylene, and amylene prepared under our own inspection, and carefully purified. The following are the results obtained :—

Ethylene Bromide.

The couple has no apparent action on ethylene bromide, unless the temperature be raised to somewhere about 115°; but even at the boiling point 129·5°, the decomposition takes place very slowly. In one experiment, 5 c.c. were boiled with a dry couple for two hours, during which time gas was evolved in a diminishing ratio; 110 c.c. were collected. On submitting the contents of the flask to distillation, undecomposed ethylene bromide passed over, without a trace of zinc-compound. From the residue in the flask, water washed out an amount of zinc bromide, which indicated that 1·18 grams of the organic bromide had suffered decomposition. The gas burnt with a very bright flame, and was almost wholly soluble in fuming sulphuric acid.

This suggested the simple reaction :—

$$C_2H_4Br_2 + Zn = ZnBr_2 + C_2H_4.$$
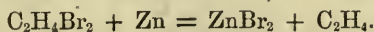
In presence of water, however, the ethylene bromide is decomposed readily at the ordinary temperature. 5 c.c. (11 grams) poured on a

couple wet with water at 15°, gave 150 c.c. of gas in the first 27 minutes, 120 c.c. in the next 5 minutes, and, though the flask was cooled by immersion in cold water, 380 c.c. in the following 15 minutes. Then the formation of gas diminished, and, after the lapse of an hour more, it ceased, the total amount collected being 1200 c.c. Water added to the product in the flask gave a very slight precipitate of zinc oxide, and a determination of the atomic ratio of the bromine to the zinc gave 1 : 0·53. The result was therefore simply bromide of zinc, for the minute excess of the metallic element may be fairly attributed to the solution, by the strong bromide, of a little oxide of zinc produced by the decomposition of water during the experiment.

The gas burnt with a luminous flame; it dissolved slightly in alcohol; it combined with bromine to form an oily body; and fuming sulphuric acid absorbed 98·3 per cent. of its volume. This indicates that olefiant gas is the sole gaseous product of the reaction, and that therefore the olefine is not hydrogenised, as is the case when the wet couple acts on bromide of ethyl. The amount of olefiant gas theoretically obtainable from 11 grams of the bromide is 1311 c.c., which agrees sufficiently well with the amount actually obtained.

Zinc alone in presence of water is capable of effecting this reaction at the ordinary temperature, but very slowly.

In presence of alcohol, the action with the couple was very violent. 5 c.c. of the bromide were mixed with 10 c.c. of absolute alcohol, and poured into a flask with the couple at 11°, evolution of gas commenced in one minute, and though the flask was at once immersed in cold water, 600 c.c. of gas were collected in the ensuing three minutes, and then the cork was blown out, and the contents of the flask projected into the room. We then had recourse to zinc alone. The same proportions of the two liquids poured on crumpled zinc-foil gave no action for nearly half an hour; but then it began, and in six minutes 140 c.c. of gas were evolved, and though the flask was kept cool, 1009 c.c. were collected within 24 minutes. The products were as before. The ratio of bromine to zinc in solution was 1 : 0·51, and the gas was soluble to 98·1 per cent. of its volume in sulphuric acid.

If the action of the couple is of the same nature whether water or alcohol be absent or present, why do these bodies facilitate the action so enormously? The answer may be sought in their removing the first product of the reaction from the surface of the zinc; for bromide of zinc is practically insoluble in the ethylene bromide, and may therefore be expected at once to form a crust, which will protect the metal from exerting any further action on the organic liquid. If this be the true state of the case, some other solvent, such as ether, which is not likely to suffer any decomposition itself, will also facilitate the reaction. 5 c.c. of the bromide, mixed with 10 c.c. of pure ether at 9°, gave no

action in 50 minutes; there was no action also at 20°; but at 40° the action was very rapid, giving 1073 c.c. of olefiant gas in 10 minutes. The action of zinc-foil on the bromide mixed with ether was very slow, even at 60° C.

That ether does facilitate the action is confirmatory of the view given above, but its small effect, as compared with that of alcohol, seems to show that the nature of the solvent also exerts some kind of physical, if not chemical influence on the reaction.

Propylene Bromide.

Two isomeric bromides of propylene have been described, the one boiling at 141°—143°, the other at 113°—116°. As we recently described a simple method of preparing propylene from iodide of allyl (p. 211 of this volume), it was of interest to us to determine which of these bromides our gas would yield. A quantity was therefore prepared and combined with bromine, and the oily product was washed with alkaline water, and dried by means of chloride of calcium. The greater part boiled at 142°—143°, and was therefore the normal propylene bromide.

When this bromide was boiled with a dry couple, very little decomposition took place, less than in the case of the ethylene compound.

Water, however, facilitated the action as before. About 2·5 c.c. (4·6 grams) of the bromide were subjected to a couple wet with water at 12°. Evolution of gas commenced at once, and continued for 24 hours, when 459 c.c. were collected. This gas burnt with a smoky flame, dissolved readily in alcohol, combined with bromine to form an oily body, and 98·9 per cent. of its volume dissolved in fuming sulphuric acid. It was therefore simply propylene, and the amount was nearly that which might have been obtained theoretically from 4·6 grams of the bromide, viz., 510 c.c.

The reaction was evidently

$$C_3H_6Br_2 + Zn = ZnBr_2 + C_3H_6.$$

Zinc-foil wetted had scarcely any action at the ordinary temperature.

As zinc alone is the preferable agent for decomposing the ethylene compound when mixed with alcohol, we tried it also in this case. 4·6 grams with 5 c.c. of absolute alcohol were added to 4·4 grams of pure granulated zinc at 15°. It was 17 minutes before visible action ensued; then it became rapid, although the flask was kept cool, and 421 c.c. of propylene gas were collected.

The effect of ether was also tried. 4·6 grams of the bromide mixed with 5 c.c. of pure ether, exposed to the couple at 40°, did not decom-

pose till after the lapse of 20 minutes; the action then proceeded some-what rapidly, yielding 455 c.c. of propylene. Zinc-foil alone, in presence of ether, produced no decomposition when the flask containing it was immersed in water at 60°.

It is evident, therefore, that a perfect analogy exists between the modes of action of the couple on the two bromides, only the more complex molecule requires the greater force to effect its separation. This is in perfect unison with what we learned while studying the ethyl and propyl iodides.

Amylene Bromide.

It was found impossible to obtain amylene bromide free from hydro-bromic acid by distillation; a specimen was therefore well washed with water, and dried by means of fused chloride of calcium.

It appeared useless to try the effect of a dry couple, especially as this bromide cannot be heated strongly without decomposition. In an experiment with the couple wet with water, there was no action in two hours at 15°; but at 60° action quickly commenced, a highly volatile liquid and bromide of zinc being produced. In presence of alcohol, zinc alone slowly effected the same decomposition at the ordinary tem-perature. The volatile liquid produced in the reaction distilled entirely at a temperature below 40°, and had the characteristics of amylene. The reaction was doubtless the same as in the lower members of the series, viz.:—

$$C_5H_{10}Br_2 + Zn = ZnBr_2 + C_5H_{10}.$$
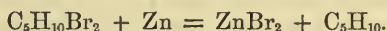
Conclusions.—It results from this inquiry that the compounds of the halogens with the dyad positive radicals, C_nH_{2n}, do not enter into com-bination with zinc in the same way as the halogen-compounds of the monad radicals, C_nH_{2n+1}.

In the one case we have the formation of a new compound, $C_nH_{2n+1}\overline{R}Zn$; in the other case a splitting up of the body into its original constituents, C_nH_{2n} and $\overline{R}_2$, which combines with zinc. In the case of the monad radicals, further reactions are easily obtained from this new compound, thus by heat:—

$$2(C_nH_{2n+1}\overline{R}Zn) = Zn\overline{R}_2 + \left.\begin{matrix} C_nH_{2n+1} \\ C_nH_{2n+1} \end{matrix}\right\} Zn,$$

or by water or alcohol:—

$$C_nH_{2n+1}\overline{R}Zn + H_2O = ZnHO\overline{R} + C_nH_{2n+2}.$$

and this reaction equally takes place if the water or alcohol is present at the time when the zinc-compound is formed.

In the case of the dyad radicals, however, the union of the zinc with the halogen splits up the original body—

$$C_nH_{2n}\overline{R}_2 + Zn = Zn\overline{R}_2 + C_nH_{2n},$$

and there is no opportunity for the formation of a zinc-olefine, or of the hydride of an olefine.
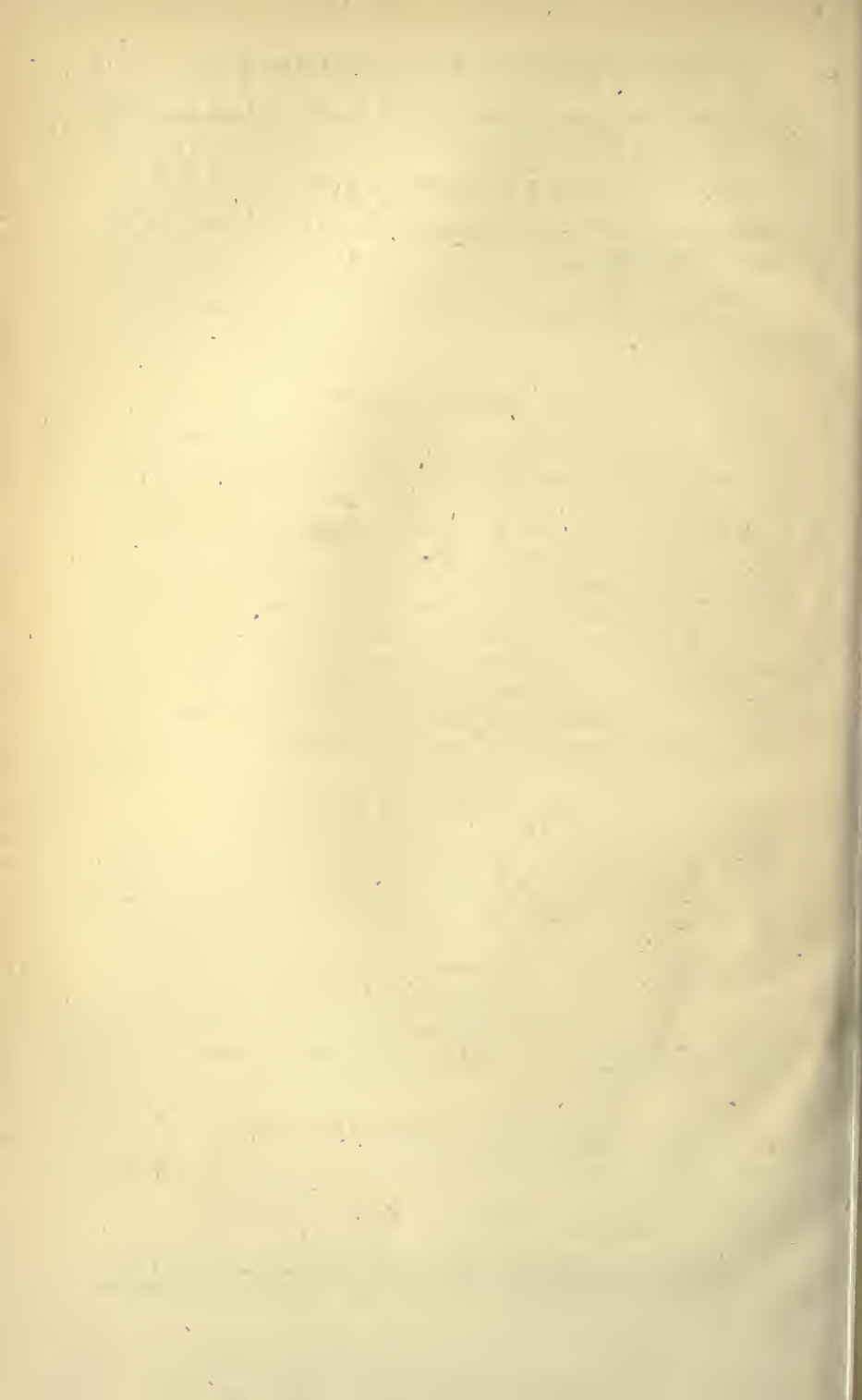
RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES. PART VI. ON ETHYL BROMIDE.

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.

AN examination of the action of our couple on ethyl bromide appeared desirable for two very different reasons. In the first place we should learn whether the behaviour of the bromide was analogous to that of the iodide, and might be able to prepare bromine analogues of zinc ethiodide and of the zinc iodo-ethylate which we described in Part I of these researches (*Journ. Chem. Soc.*, 1873, pp. 445—452). In the second place, as the bromide is much cheaper than the iodide of ethyl, and contains more of the organic radical, we hoped it might afford a method of preparing zinc-ethyl at a smaller cost.

According to Pierre, the boiling point of ethyl bromide is 40·7° when the barometer stands at 757 mm., and the specific gravity is 1·4733 at 0°. Our experience has been somewhat different. We examined three specimens.

Specimen I, made by Hopkin and Williams by the action of phosphorus bromide, after rectification and drying, boiled at 38°—39°, bar. 760 mm. Its specific gravity was 1·385 at 15°.

Specimen II, made by Hopkin and Williams by acting on pure alcohol with strong hydrobromic acid, boiled at 38·5°—39·5°. Its specific gravity was 1·47 at 15°.

Specimen III, made by ourselves by acting on alcohol with phosphorus and bromine, boiled also at 38·5°—39·5°.

Action of the Dry Couple on the Bromide.

The action between the copper-zinc couple and the bromide appears to depend on small differences of condition, the nature of which we have not been able satisfactorily to determine.

In one experiment 5 c.c. (about 7·3 grams) of the specimen prepared by means of bromide of phosphorus, were boiled with a dry couple in

the usual way, and in 14 hours the return flow had ceased, and the action appeared complete. In the flask, mixed of course with the copper and remaining zinc, was a white crystalline body, which effervesced on addition of alcohol, and was violently decomposed by water with formation of zinc bromide and oxide. This crystalline body yields zinc-ethyl when heated. It dissolves readily in ether, but the ether separates only imperfectly from it by evaporation *in vacuo* over sulphuric acid, leaving a viscid mass. In a portion of this the atomic ratio of bromine and zinc was determined, and found to be $1 : 0.983$. There can be no doubt, therefore, that the crystalline body produced was zinc ethylobromide, $\left.\begin{array}{l} C_2H_5 \\ Br \end{array}\right\} Zn$, the analogue of Frankland's ethiodide.

In Part I we showed that the iodine-compound could be prepared by gently heating zinc-ethyl and zinc iodide together. We found that this bromine-compound could also be formed in a similar way. It melts at 62°, and crystallises on cooling in white pearly scales.

In another experiment 5 c.c. of the same specimen of bromide were heated with a couple in a water-bath at 55°. In 36 hours the return flow ceased. The flask was gently heated over a gas-flame, and the zinc-ethyl produced was distilled over in a current of carbonic acid gas into water. The zinc oxide obtained amounted to 0.606 gram, which, however, is equivalent only to 1.63 gram of ethyl bromide. This small yield led us to determine the amount of bromine which had combined with zinc during the experiment, and we found it to indicate the decomposition of 4.4 grams of the ethyl compound. It is evident, therefore, that the bulk of the product is lost through the conversion of the ethylic element into permanent gases.

In an experiment similar to the last in every respect, as far as we know, no action whatever took place in 36 hours.

In two other experiments, performed simultaneously and in a perfectly similar manner, the return flow ceased in about 40 hours. Ethylobromide of zinc was produced in each case, but in different quantity; for on decomposing the one with water and the other with alcohol, 400 c.c. of ethyl hydride were evolved in one case, and 750 c.c. in the other. This shows that in the first about one-fourth of the possible amount of ethylobromide had been produced, in the second nearly a half.

Another pair of experiments was made with specimens II and III of the ethyl bromide. No action in 36 hours in either case.

These contradictory results led us to inquire whether the action had been started by the presence of some moisture or a trace of alcohol. Two simultaneous experiments were therefore made with two portions of 5 c.c. each of specimen II, the one portion being saturated with

water, the other mixed with 0·5 gram of absolute alcohol. In 20 hours there was no action in the first, while in the second the return flow had greatly diminished. On opening the flask, fumes were produced, and on heating it over a lamp, zinc-ethyl mixed with some ethyl bromide distilled. The zinc-ethyl gave 0·058 gram of zinc oxide, equivalent to ·013 gram of the original bromide, but the amount of bromine in combination with zinc in the flask showed that 3·4 gram of the original substance had been acted upon. The alcohol present was sufficient to destroy the ethylobromide produced from 1·18 gram, and if it really started the action, it is evident that the action was continued afterwards without its intervention.

Action of the Couple upon Ethyl Bromide mixed with a small quantity of Ethyl Iodide.

Our earliest experiments on ethyl bromide were made with a specimen that boiled at 40°—42°,—the boiling point given in the books being 40·7°,—but which we afterwards found to contain 3·1 per cent. of ethyl *iodide*. The reaction always took place with this specimen, and with comparative rapidity. We can scarcely be wrong in supposing that the ethiodide was first formed, which facilitated the formation of the ethylobromide. In three experiments the following quantities of zinc-ethyl were obtained:—

	C_2H_5Br used.	Duration of first heating.	ZnO obtained.	Equivalent to $C_4H_{10}Zn$.
No. 1....	7·4 grams.	11 hours.	0·908	1·39 gram.
„ 2....	„	10.5 „	0·875	1·33 „
„ 3....	„	10 „	—	1·48 „

As the amount of zinc-ethyl theoretically obtainable from 7·4 grams of the bromide is 4·17 grams, it is evident that the loss amounts to two-thirds of the whole. In order to see where this occurs, the third experiment was carried out with great care. The ethylobromide was heated in a paraffin bath at 240°, and the gas evolved in each operation was collected. This gas burnt with a very bright flame and formed an oily body with bromine. Fuming sulphuric acid absorbed 48 per cent. of its volume, leaving a gas which also burnt luminously.

We concluded, as in the case of the ethyl *iodide*, that this gas consisted of ethylene and ethyl hydride in equal volumes.

The 7·4 gram of ethyl bromide may be thus accounted for:—

Vapour carried over with the gas
    during the first heating . . . . $= 1.08$ grams.
100 c.c. of gas during first heating $= 0.48$,,
515 c.c. of gas during the heating
    of the ethylobromide   . . . . $= 2.50$,,
1.48 gram of zinc ethyl . . . . $= 2.60$,,
Gas dissolved in water, and other
    loss. . . . . $= 0.74$,,

                                      7.4 ,,

It is evident that in this experiment the ethylobromide split up by heat according to the two following equations in about equal proportions :—

$$2 \left.{C_2H_5 \atop Br}\right\} Zn = ZnBr_2 + Zn + C_2H_6 + C_2H_4.$$

$$2 \left.{C_2H_5 \atop Br}\right\} Zn = ZnBr_2 + \left.{C_2H_5 \atop C_2H_5}\right\} Zn.$$
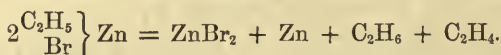
It is probable that the greater destruction of the bromine-zinc compound by heat than in the case of the analogous iodine-zinc compound is caused by the higher temperature at which the reaction takes place.

As a method of preparing zinc-ethyl, it is evident that bromide mixed with a little iodide may be employed, but it can be economically employed only in those cases where the zinc salt produced is thrown away. For manufacturing purposes it would be less advantageous than the process we formerly described.

Action of the Couple on Ethyl Bromide and Water or Alcohol.

The action in presence of water or alcohol, at the ordinary temperature is very slow.

5 c.c. of the bromide were added to a copper-zinc couple wet with water at 11°. Evolution of gas soon commenced, but in 24 hours only 100 c.c. had collected. The gas had the properties of ethyl hydride; and the flask contained bromide and oxide of zinc.

5 c.c. of the bromide were added to a couple wet with absolute alcohol at 11° C. Evolution of gas did not commence for three hours, and then it proceeded at the rate of about 5 c.c. per hour.

5 c.c. (7.3 grams) of the bromide were mixed with 10 c.c. of absolute alcohol, and added to twice the usual quantity of couple. The flask was heated by immersion in water at 55° for six hours, and at 75° for two hours more, when evolution of gas ceased: 955 c.c. had been collected, and it had the properties of hydride of ethyl. The product in the flask was semi-fluid; and the addition of water to it

produced bromide of zinc with a copious precipitate of zinc oxide. The amount of bromine in combination with zinc showed that 5·07 grams of the ethyl-compound had been decomposed, which would be equivalent to 1041 c.c. of gas.

In order to study this new product more fully, another portion was prepared in the same way and separated from the metals in the flask by solution in alcohol and filtration. This alcoholic extract was colourless. A portion was used for determination of the atomic ratio between the zinc and bromine, which was found to be—

$$1 : 1·025.$$

Another portion was heated at 100° in a distilling flask, but this temperature was found insufficient to drive off all the alcohol, though it was becoming yellowish and viscid. It was then kept at 200° for an hour, which did free it from the alcohol, but at the same time turned it brownish yellow. It was semi-solid at 200°, and quite solid at the ordinary temperature. A determination of the bromine in a portion of this indicated 45·55 per cent., which is somewhat higher than pure $\left.\begin{array}{c} C_2H_5O \\ Br \end{array}\right\}$ Zn would give, viz., 42·1 per cent. On heating another portion gently over a flame, it blackened, with separation of metallic zinc, and gave off a little combustible gas, and the odour of ether.

From the close analogy of these properties to those of the iodo-ethylate of zinc, which is produced in a precisely similar way from the iodide of ethyl, there can be no reasonable doubt that this body is the brom-ethylate of zinc, $\left.\begin{array}{c} C_2H_5O \\ Br \end{array}\right\}$ Zn.

The action of water is easily understood—

$$2\left.\begin{array}{c} C_2H_5O \\ Br \end{array}\right\} Zn + H_2O = ZnBr_2 + ZnO + 2C_2H_6O.$$
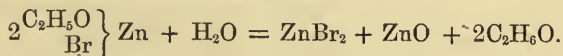
If it is really ether that is produced from it by the action of heat, that may arise simply from the reaction of two molecules :—

$$2\left.\begin{array}{c} C_2H_5O \\ Br \end{array}\right\} Zn = ZnBr_2 + ZnO + C_4H_{10}O.$$

Conclusion.

These results are perfectly analogous to those we obtained when studying the action of the couple on the iodide of ethyl. They are moreover in perfect accordance with the ordinary belief that a bromid is a more stable compound than an iodide.

The view we are disposed to take of the reactions is as follows :— The bromide of ethyl attacking the metal gives rise in all cases to the

ethylobromide of zinc, $\left.\begin{matrix} C_2H_5 \\ Br \end{matrix}\right\}$ Zn.   When this is heated by itself, two molecules react on one another or redistribute their elements with production of zinc bromide and zinc-ethyl, or the ethyl molecules may also redistribute their elements, with formation of the gases C_2H_6 and C_2H_4.   When, however, water is present at the moment of formation of the ethylobromide of zinc, or is added afterwards, it suffers the simple decomposition :—

$$\left.\begin{matrix} C_2H_5 \\ Br \end{matrix}\right\} Zn \ + \ H_2O \ = \ \left.\begin{matrix} HO \\ Br \end{matrix}\right\} Zn \ + \ C_2H_6 \, ;*$$
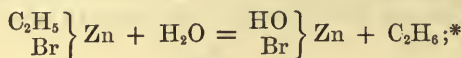
while alcohol under similar circumstances effects a similar change—

$$\left.\begin{matrix} C_2H_5 \\ Br \end{matrix}\right\} Zn \ + \ \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O \ = \ \left.\begin{matrix} C_2H_5O \\ Br \end{matrix}\right\} Zn \ + \ C_2H_6.$$
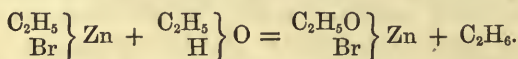
This explanation is applicable to all the analogous reactions formerly described where the copper-zinc couple attacks the iodides of ethyl, methyl, amyl or propyl; and we believe it to be the true explanation, since it disposes of the difficulty why alcohol should give up its hydrogen to the organic radical, though it is not itself capable of being decomposed by the couple.

* We have here assumed the formation of an oxybromide of zinc, as Frankland has assumed that of an oxyiodide under similar circumstances; but it has never been seen, as the excess of water always forms a mixture of zinc bromide and zinc hydrate.

RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES. Part VII. ON THE CHLORIDES OF ETHYLENE AND ETHYLIDENE.

By J. H. Gladstone, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and Alfred Tribe, F.C.S.

Among the haloïd compounds belonging to the group which we have been recently examining by means of the copper-zinc couple, are two well-defined isomeric bodies, having the composition $C_2H_4Cl_2$, the one the chloride of ethylidene, the other the chloride of ethylene. We obtained specimens of each. That of the first was prepared by Messrs. Schuchardt, by combining chlorine and chloride of ethyl. It distilled very uniformly at a temperature of 61°. Its specific gravity was 1·201 at 13°, and its refractive index for A, 1·4183. Two specimens of chloride of ethylene were rectified by distillation; that with the steadiest boiling point (1) had a specific gravity of 1·272 at 14°, and its refractive index for A was 1·4448. The refraction-equivalent of the ethylidene compound was therefore 34·6, that of the ethylene compound 34·5. The two isomeric bodies are, therefore, evidently the same in this respect.*

The dry copper-zinc couple was found to have little or no action on either chloride, even at its boiling point; but in presence of water there is a small action in each case, and in presence of alcohol a more energetic one, at least in the case of the ethylidene compound.

Action in presence of Water.

5 c.c. (6·04 grm.) of chloride of ethylidene were poured on a couple wet with water at 15°. Evolution of gas was perceptible after the lapse of an hour, and in 24 hours 52 c.c. were collected. The flask was then immersed in a water-bath at 50°, and in seven hours 162 c.c. were evolved. The gas burnt with a luminous flame, but did not form an oily body with bromine. The liquid in the flask was principally the undecomposed ethylidene compound, with a little chloride and oxide of zinc.

* The refraction-equivalent of $C_2H_4Cl_2$, deduced from the values previously assigned to its elements previously determined, would be 35·0.

A precisely similar experiment was made with chloride of ethylene. The gas collected in 24 hours at the ordinary temperature was 57 c.c.; that collected in seven hours at 50° was 95 c.c. It gave little light when burnt, and did not combine with bromine. The flask again contained a small quantity of chloride and oxide of zinc.

Action in presence of Alcohol.

Neither of these isomeric chlorides when mixed with alcohol is attacked readily by the couple at the ordinary temperature, but in the case of the ethylidene compound the action is moderately rapid near its boiling point.

5 c.c. of this were mixed with twice the bulk of absolute alcohol, and added to twice the usual quantity of the couple. The flask was heated in a bath at 60°—62° for ten hours, and at 80° for three hours more, when no further gas was evolved. The amount collected was 932 c.c. The chlorine combined with zinc in the flask was found to be equivalent to 4·82 grams of ethylidene chloride, from which it would be possible to obtain 989 c.c. of gas.

The substance in the flask was not, however, oxide of zinc. It was a viscid liquid, readily soluble in absolute alcohol, from which solution water precipitates zinc oxide in large quantity. The atomic ratio between the zinc and the chlorine was determined in three different specimens, and found to be—

Zn.		Cl.
1	:	1·08
1	:	1·08
1	:	1·09

On distilling the alcoholic solution in a water-bath at 100°, a viscid liquid was obtained, which gave off more alcohol when heated to 200°, and left a yellowish-brown solid. When this was heated at a still higher temperature, it split up into zinc oxychloride, metallic zinc, carbon, some combustible gas, and a small quantity of a brown oily liquid possessing an ether-like odour.

These properties are not precisely analogous to those of the zinc iodoethylate and bromethylate, previously described by us (*Journ. Chem. Soc.* [2], xi, 452; xii, 414), but they leave little room for doubt that the compound is the corresponding zinc chloroethylate—

$$\left.\begin{array}{c} C_2H_5O \\ Cl \end{array}\right\} Zn.$$
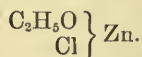
The gas produced by the action of the couple was washed by passing it through bulbs containing alcohol and water, and was analysed by Bunsen's method. Nordhausen sulphuric acid absorbed 5·2 per cent.

of its volume. After removal to the eudiometer the following were the data obtained :—

	Volume observed.	Tempera- ture.	Difference of high level.	Barometer.	Vol. at 0° and 1 m.
Gas used (moist)......	25·824	16° C.	416	766·32	8·374
After adding air and O. (moist)	304·754	13	137	767·08	180·34
After combustion (moist)	286·443	14·8	155·8	759·20	160·73
After absorption of CO_2 (dry).............	263·005	14	178·1	756·41	144·95

These numbers give the following results :—

<div align="center">

Gas burnt .... 8·374

Contraction............ 19·61

Carbonic anhydride .... 15·78

</div>

The ratio of contractions due to CO_2 and H_2O, therefore, was—

$$1 : 1·242$$

As the ratio in the combustion of C_2H_6 would be—

$$1 : 1·25$$

hydride of ethyl is clearly indicated.

The action of the couple upon chloride of ethylidene and alcohol would appear, therefore, to be very simple, namely :—

$$C_2H_4Cl_2 + 2{C_2H_5O \atop H} \Big\} + 2Zn = C_2H_6 + 2{C_2H_5O \atop Cl} \Big\} Zn.$$
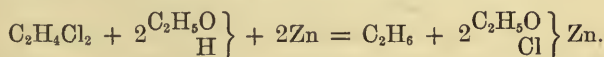
But the 5·2 per cent. of gas absorbable by sulphuric acid, and the slight excess of chlorine above what is required by the chloro-ethylate, would indicate a small amount of decomposition according to the reaction—

$$C_2H_4Cl_2 + Zn = C_2H_4 + ZnCl_2.$$

From what we had already learnt by the study of the iodide and bromide of ethyl, it might have been fully expected that hydride of ethyl and chloro-ethylate of zinc would be formed from chloride of ethyl and alcohol, if the experiment could be made; but it could scarcely have been expected beforehand that the replacement of an atom of hydrogen by one of chlorine would have no further effect upon the result than the formation of a second molecule of chloro-ethylate of zinc. The intermediate formation of chloride of ethyl is not improbable, and would explain everything.

The behaviour of chloride of ethylene is very different.

5 c.c. of the chloride mixed with 10 c.c. of absolute alcohol, were heated with twice the usual quantity of couple at 80°. Within twenty minutes 80 c.c. of gas were evolved, but no more made its appearance, although the heating was continued for five hours. In another experiment, made with a different specimen of the chloride, only 41 c.c. of gas were obtained, and the half of that came within the first ten minutes. In the first experiment, the amount of chlorine combined with zinc showed that 0·743 gram of the ethylene compound had undergone decomposition; in the second experiment 0·33 gram. The addition of water to the liquid in the flask gave but a very slight precipitate of zinc oxide, and the ratio between the zinc and the chlorine was found to be—

$$\text{Exp. 1} \quad \ldots\ldots\ldots \quad 1 : 1\text{·}89$$
$$2 \quad \ldots\ldots\ldots \quad 1 : 1\text{·}93$$

This investigation of the action of the copper-zinc couple on the two isomeric bodies $C_2H_4Cl_2$ has therefore enabled us to do two things—

1st. To show their chemical difference, and to support the view that the one is really monochlorinated chloride of ethyl, $C_2H_4Cl.Cl$, while the other is the dichloride of the dyad radicle ethylene, C_2H_4,Cl_2.

2nd. To complete the series of zinc haloïd ethylates—

$$\left. \begin{array}{c} C_2H_5O \\ I \end{array} \right\} Zn, \qquad \left. \begin{array}{c} C_2H_5O \\ Br \end{array} \right\} Zn, \qquad \left. \begin{array}{c} C_2H_5O \\ Cl \end{array} \right\} Zn.$$
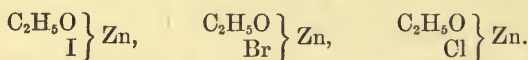
RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES.—PART VIII. ON CHLOROFORM, BROMOFORM, AND IODOFORM.

By J. H. GLADSTONE, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and ALFRED TRIBE, F.C.S., Lecturer on Chemistry in Dulwich College.

IN our earliest description of the power of the copper-zinc couple we stated that it was capable of decomposing chloroform. We have lately examined its action upon this body, and the analogous bromine and iodine compounds.

CHLOROFORM.

The dry couple was found to have no action upon this substance either when alone or in presence of pure ether.

In presence of *absolute alcohol* no action was observed at the ordinary temperature. At about 50° C., however, action takes place, and in a few minutes proceeds rapidly.

In one experiment 5 c.c. of chloroform (7·5 grams) were mixed with 20 c.c. of absolute alcohol, and the mixture added to twice the usual quantity of couple. No action was observable in one hour (temp. 12° C.). The temperature was now raised to 60°. In five minutes 20 c.c. of gas had collected, and in the next three minutes 50 c.c. (The action had now become so rapid, and the temperature had risen so considerably in consequence, that it was necessary to agitate the flask in cold water.) In the next five minutes 680 c.c., and in the next two minutes 180 c.c., had collected; in another four minutes the action was practically over. The quantity of gas collected during the 19 minutes amounted to 984 c.c. (corrected).

The chlorine in combination with zinc was determined in the usual way, and found to be equivalent to 5·92 grams of CHCl$_3$, which would

1,109 c.c. of marsh-gas, assuming the three atoms of chlorine to have been replaced by hydrogen.

In another similar experiment, with equal quantities of material, the contents of the flask were heated to 20° C. for 15 minutes. No action took place. At 50° action commenced and quickly became very violent. In 15 minutes action was practically over, 967 c.c. having been collected.

The gas, after being washed with alcohol and water, possessed the general properties of methyl hydride.

The product remaining in the flask was very viscid, and very soluble in alcohol. Water added to the alcoholic solution produced a copious precipitate of ZnH_2O_2. The atomic ratio of zinc to chlorine was determined and found to be $1 : 1·08$.

The product, after the removal of alcohol by distillation, behaved just as the chloro-ethylate of zinc which we obtained by the reaction—

$$C_2H_4 \left.{Cl \atop Cl}\right\} + 2{C_2H_5O \atop H}\Big\} + 2Zn = {C_2H_4H \atop H}\Big\} + 2{C_2H_5O \atop Cl}\Big\} Zn,$$
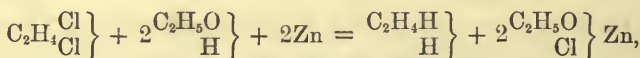
and described by us in the Society's Journal for May, 1874.

Subsequent experiments upon bromoform and iodoform induced us to suspect the formation of some acetylene during the action of the couple upon chloroform in presence of alcohol. Another experiment was therefore made similar to those already described, the gas being passed through a solution of cuprous chloride in ammonia. Some of the red acetylene compound which on analysis gave ·0689 Cu, equal to 12 c.c. acetylene or ·1296 gram chloroform.

Taking the above facts into consideration, we may conclude that about 92 *per cent.* of the action may be represented by the equation—

$$CHCl_3 + 3{C_2H_5O \atop H}\Big\} + 3\,Zn = CH_4 + 3\left\{{C_2H_5O \atop Cl}Zn,\right.$$
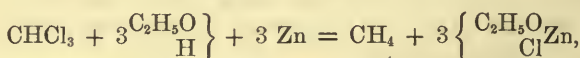
and a small percentage by the equation—

$$2CHCl_3 + 3Zn = C_2H_2 + 3ZnCl_2.$$
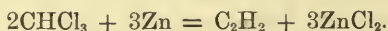
We tried the action of the couple in the presence of water. 5 c.c. were added to the usual quantity of couple wet with water, temperature 12° C. Gas was at once slowly evolved. The temperature of the contents of the flask rose somewhat in the first 20 minutes, and the action became more rapid. In the first hour 170 c.c. of gas had collected; in the second, 60 c.c.; in the third, 35 c.c.; and so on, in a diminishing ratio. At the end of four days the action was no longer going on. The total gas collected measured 626 c.c.

The couple remaining in the flask was coated with a white substance, which was found to be oxychloride of zinc, the formation of

which in all probability prevented the completion of the reaction, and accounts for its rapid falling off. The gas burnt with a flame like marsh-gas.

The reaction may therefore be represented thus—

$$2CHCl_3 + 3H_2O + 6Zn = 2CH_4 + 3(ZnCl_2ZnO).$$
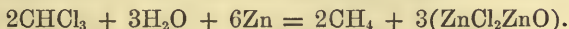
From these results it might be expected that with aqueous alcohol the reaction would take place at a lower temperature than when absolute alcohol is employed. Such was found to be the case. An experiment was made with 5 c.c. of chloroform mixed with 15 c.c. of absolute alcohol and 5 c.c. of water, added to twice the usual quantity of the dry couple. Evolution of gas commenced immediately, and in a few minutes the contents of the flask had sensibly risen in temperature. 150 c.c. of gas collected during the first ten minutes, and the action continued in a diminishing ratio for about 24 hours, when it was found that 438 c.c. had collected.

Oxychloride of zinc was found adhering to the remaining couple, which probably stopped the action, as on the addition of more water the action did not recommence.

Zinc-foil was found not to have an action on chloroform mixed with absolute alcohol at 60° C., but at the boiling-point of the mixture there is a slow action, CH_4 and ${C_2H_5O \atop Cl}\Big\}Zn$ (chloroethylate of zinc) being produced.

Zinc-foil was also found slowly to act upon chloroform mixed with alcohol diluted with one-fourth of its volume of water at 50° C., zinc oxychloride and CH_4 being the principal products.

It is evident that the reactions described above afford a ready method of preparing marsh-gas.

BROMOFORM.

Action of the Couple in presence of Alcohol.

If the couple be in a finely divided condition, this reaction takes place after a minute or two with almost explosive violence. It was found necessary, therefore, in order to study the reaction, to employ a coarse couple.

It was found that the gas produced by the reaction burnt with a very luminous flame. This led us to suspect the presence of some olefiant gas or acetylene, and accordingly the gas was passed through an ammoniacal solution of cuprous chloride. A quantity of a red precipitate formed which when washed and dried detonated upon heating, and had all the other properties of copper acetylide.

In one experiment 2·5 c.c. (7 grams) were added to 20 c.c. of absolute alcohol, and the mixture was added to the usual quantity of dry

couple. Action commenced at once at the ordinary temperature, and the liquid soon becoming hot, it proceeded very rapidly. The flask was kept agitated in cold water. In seven minutes the evolution of gas had ceased.

The gas produced in the reaction, after passing through a solution of ammoniacal cuprous chloride, measured 190 c.c. It did not combine with bromine, and burnt with an almost non-luminous flame, yielding carbonic anhydride. Determination of copper in the red precipitate gave ·334 gram of copper.

The product of the reaction left in the flask possessed the general properties of the bromoethylate of zinc previously described by us, and gave on determining the atomic ratio of zinc to bromine 1 of the former to 1·5 of the latter. The total zinc found in combination with bromine was equivalent to 6·5 grams of bromoform.

In another experiment 203 c.c. of non-absorbable gas were obtained, and ·333 gram of copper in the copper acetylide precipitate. The ratio of zinc to bromine was 1 : 1·48.

Now, taking the mean of the above results, we have—

	Grams.	
Gas possessing the properties of marsh-gas, equivalent to	2·21	of bromoform.
Gas forming a red precipitate with ammoniacal cuprous chloride, calculated as acetylene....	1·33	,,
Total accounted for by gaseous products......	3·54	,,

That nearly the whole of the bromoform undergoes decomposition is evident from the amount of bromine found in combination with zinc in the flask. But what becomes of the CH of the $CHBr_3$, corresponding to nearly 3 grams?

Thinking that benzene a polymeride of acetylene (C_6H_6), might have been produced and retained in the flask, that substance was sought for, but only with a negative result. In fact till recently the whereabouts of this CH remained a mystery, but it was explained when we came to experiment with iodoform.

The ratio of zinc to bromine would point to the reactions—

$$(a.) \ \ CHBr_3 + 3{C_2H_5O \atop H}\Big\} + 3Zn = CH_4 + 3{C_2H_5O \atop Br}\Big\} Zn,$$

$$(b.) \ \ 2CHBr_3 + 3Zn = C_2H_2 + 3ZnBr_2,$$
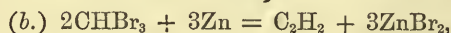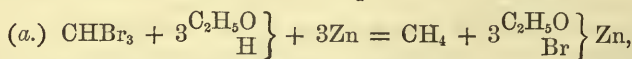
as having taken place in about equal proportions, but the ratio of acetylene to marsh-gas would seem to show that nearly two-thirds of the bromoform was decomposed according to the reaction (a), the other third being according to reaction (b).

Zinc-foil.—2·5 c.c. (7 grams) of bromoform were mixed with 20 c.c.

of alcohol and added to the usual quantity of zinc-foil in small pieces. No apparent action was observable in 30 minutes at a temperature of 40° C., only a slight action at 50°, but after a few minutes' heating at 60° the evolution of gas became very rapid, and the action ceased in about 30 minutes.

Examination of the products gave—

	Grams.
Gas non-absorbable by ammoniacal cuprous chloride 521 c.c., equivalent to	5·88 of bromoform.
Gas absorbable by the same, equivalent to ..	0·13 ,,
Bromine combined with zinc, equivalent to..	6·67 ,,

The ratio of zinc to bromine was found to be as 1 to 1·17.

Comparing the respective actions of the couple and of zinc upon bromoform and alcohol, there is noticeable not only a difference in the degree of action of the two agents, but also in the relative amounts of the two hydrocarbons produced. Thus with zinc, acetylene appears in much smaller quantity, while marsh-gas is produced in very much greater quantity. Also with zinc there is no CH unaccounted for, as was the case when the couple was employed.

Bromoform. Couple and Water.

At the ordinary temperature action takes place very slowly, CH_4 being evolved and zinc bromide and oxybromide formed. At 60° C. the action is of course more rapid, and the CH_4 is found mixed with a very little acetylene.

IODOFORM.

Couple in presence of Alcohol.

Action takes place at the ordinary temperature of the air, but extremely slowly. This may be due in part to the slight solubility of iodoform in alcohol. At 40° C. the action is perceptible, and with agitation quickly becomes somewhat rapid.

In one experiment 8·45 grams of iodoform and 10 c.c. of absolute alcohol were added to the couple, and the whole heated to 40° C. by immersion in water at that temperature. The evolution of gas ceased in 25 minutes. It contained a large proportion of acetylene.

The gas non-absorbable by ammoniacal cuprous chloride measured 226 c.c., which is equivalent to	3·97 grams CHI_3
The copper in the acetylene precipitate weighed 0·375 gram, equivalent to......	2·32 ,,
	6·29 ,,

The ratio of zinc and iodine in the semi-fluid product remaining in the flask was 1 of zinc to 1·41 of iodine.

Zinc-foil.—In one experiment 8·6 grams of iodoform mixed with 10 c.c. of alcohol were added to about 9 grams of zinc-foil crumpled and in small pieces. A very slow action was observable at 50° C., but at the boiling-point of the alcohol the action was rapid, being completed in about ten minutes.

The gas non-absorbable by cuprous solution measured 377 c.c., equivalent to .... 6·63 grams CHI_3.
The copper in acetylene precipitate was equivalent to .... 1·29   ,,

$$\overline{7·92}$$,,

The ratio of zinc to iodine in the product of the reaction in the flask was 1 : 1·11, which would appear to indicate that about 89 per cent. of the substance had been decomposed according to the equation—

$$CHI_3 + 3{{C_2H_5O}\atop{H}} \Big\} + 3Zn = CH_4 + 3Zn\Big\{ {{C_2H_5O}\atop{I}}.$$
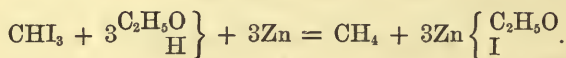
We remark here, as we previously remarked when speaking of bromoform, that the couple gives a greater proportion of the acetylene reaction than does zinc alone; and also, that practically the whole of the CH in the iodoform is accounted for when zinc is employed, whereas a considerable proportion of those elements apparently disappears when the couple is used.

The fact that the loss of CH occurs only when the couple is used led us to think that the CH would be found in combination with the copper of the couple. The following experiment with iodoform was consequently made :—

5 grams of iodoform and 10 c.c. of alcohol were heated with a proportional quantity of couple. After the reaction, the solid residue in the flask was washed with alcohol, then with water dried over sulphuric acid *in vacuo*, and finally burnt with copper oxide. 0·166 gram of CO_2 was obtained, which is equivalent to 1·487 gram of iodoform, a quantity closely corresponding to that which we had been unable to account for. It is to be presumed that it existed as acetylide of copper.

Thinking that a greater yield of gaseous acetylene might be obtained by using platinum, with which acetylene is not known to combine, we employed a zinc-platinum couple. We found that the reaction with iodoform and alcohol took place at a lower temperature and was more

energetic, but about the same proportion of CH_4 to C_2H_2 was obtained as with the copper-zinc couple, and also about the same amount of loss. Carbon was found in the insoluble residue, but whether as acetylide or some polymeride of acetylene it is difficult to say.

Conclusion.

In presence of alcohol the three bodies are split up in the same general manner, acetylene and marsh-gas being the hydrocarbon products in addition to the haloïd zinc-ethylates previously described by us. In the cases of chloroform and bromoform there is noticeable a marked difference in their activity, the latter being, as we might expect, the more energetic. The insolubility of iodoform in alcohol prevents us from drawing any conclusion as to its comparative activity. There is also a gradation in the proportion of acetylene. Thus 1·7 per cent. of chloroform, 19 per cent. of bromoform, and 27·4 per cent. of iodoform were converted into this body.

THE ELECTROLYSIS

OF

CERTAIN METALLIC CHLORIDES.

BY

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AND

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WE have previously shown that nitrate of copper brought into tension by silver and copper in conjunction is decomposed by free oxygen in solution[†]. Thinking that chlorine might be substituted for oxygen, we commenced some experiments, employing chloride of copper, and observed some facts which seemed to have an interest from their bearing on the causation of galvanic action.

It is known that if metallic copper be placed in a solution of cupric chloride, it will slowly become covered with a crystalline deposit of the insoluble cuprous chloride:—

$$Cu + CuCl_2 = 2CuCl.$$
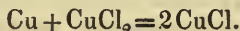
We found that when metallic copper and platinum are connected by a wire and immersed in cupric chloride, the insoluble salt forms not only upon the copper, but also on the platinum plate, as a white crystalline body. This deposit may generally be observed in about two minutes when the plates are three quarters of an inch apart. The formation of cuprous chloride upon the platinum plate takes place about equally rapidly in solutions containing 2·5 or 10 per cent. of salt. With a 20 per cent. solution the deposit was smaller, and with 40 per cent.

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[*] Read before the Physical Society, 1875.
[†] Proc. Roy. Soc. vol. xx. p. 290.

practically *nil,* although there was abundant formation of cuprous chloride upon the *copper* plate.

We satisfied ourselves that the action took place equally well in solutions from which oxygen had been rigidly excluded, and also that a current passed from the copper to the platinum through the liquid—that is, from the metal of higher to that of lower potential.

In order to test whether this electrolysis of cupric chloride into CuCl and Cl could be effected by weak currents *ab extra*, we tried the effect of a zinc-platinum cell excited by common water and with platinum electrodes, and found that cuprous chloride deposited upon the negative electrode and chlorine at the positive, a little of which entered into combination with the platinum, but the greater part passed into the liquid. A cell excited with dilute sulphuric acid acted in a similar manner. A single Grove's cell gave for the first two or three minutes cuprous chloride on the negative platinum electrode, but afterwards metallic copper, while chlorine always formed at the positive plate.

As zinc immersed in a salt of copper is capable of throwing down that metal, an experiment was tried with plates of zinc and platinum in connexion immersed in the chloride; the result was a more energetic action than with a copper-platinum couple similarly arranged, and besides a thick coat of cuprous chloride the edges of the platinum were incrusted with metallic copper. A similar magnesium-platinum couple gave a similar result, but with a decidedly greater proportion of metallic copper.

As there are two chlorides of mercury, similar to the two chlorides of copper, analogous experiments were tried with solution of corrosive sublimate.

A small bell-jar which terminated in a corked orifice was inverted and partly filled with mercury, over which was poured a solution of mercuric chloride; a wire passed from the mercury through the cork to a plate of platinum which hung in the solution, without, however, touching the mercury. On pouring the mercuric chloride upon the mercury, the metallic surface was at once dimmed by a film of mercurous chloride, which increased in quantity; and in the course of an hour or two the insoluble chloride appeared also on the platinum plate, and in twenty-four hours it was sufficiently thick to permit of its removal. On repeating this experiment with gold instead of platinum, the same mercurous chloride was deposited; but at the same time the gold plate was amalgamated, showing that the reduction of the mercuric chloride had not stopped at the first stage, but had actually proceeded to the separation of the metal itself. A similar gold plate immersed in the same solution of corrosive sublimate, but not in connexion with the mercury, showed no trace of de-

posit or amalgamation ; and it was ascertained that gold alone has no power of decomposing moistened mercurous chloride.

An experiment was made with a current *ab extra*. A cell of Grove's was found to decompose mercuric chloride with the formation of the mercurous compound at the negative platinum electrode, while chlorine was given off at the positive one. This is in unison with what was found in the case of the copper salts.

That this action does not depend on the insolubility of the *-ous* chlorides was proved by the behaviour of the iron salts. Ordinary metallic iron is capable of reducing the ferric to the ferrous salt at the common temperature ; thus :—

$$2\,FeCl_3 + Fe = 3\,FeCl_2.$$
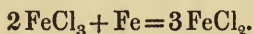
Platinum does not effect such a reduction ; but when the iron is connected with platinum the change takes place more rapidly, and the reduced salt forms also on the negative metal. This, of course, does not render itself evident by any deposit, nor by any appreciable change of colour at first ; but if the platinum plate be lifted out of the solution, and the liquid clinging to it be allowed to drain on to a paper moistened with some ferridcyanide of potassium, Turnbull's blue is the result. Or if a few drops of the ferridcyanide be mixed with the solution of the ferric chloride, on the junction of the iron and platinum the blue colour makes its appearance against each metal. Of course care was taken that the original salt contained no acid. The solution employed was one of 3·5 per cent. in strength.

If plates of magnesium and platinum be immersed in ferric chloride, metallic iron quickly makes its appearance on the platinum plate.

With a weak external battery and platinum electrodes the salt was resolved into chlorine and ferrous chloride, but with a strong battery into chlorine and iron—thus affording another instance of the close analogy between the primary electrolysis produced in the cell itself, and the secondary electrolysis that may be produced by an external battery.

On the Replacement of Electro-positive by Electro-negative Metals
in a Voltaic Cell. By J. H. Gladstone, Ph.D., F.R.S.,
Fullerian Professor of Chemistry in the Royal Institution, and
Alfred Tribe, Esq., Lecturer on Chemistry in Dulwich Col-
lege.

It is well known that one metal exerts a greater chemical force than
another, and is capable of displacing it from its combinations. Among
those metals with which we are familiar, potassium is looked upon as the
most powerful; and it is a certain fact that calcium, barium, strontium,
aluminium, and magnesium have been isolated by its agency. It could
scarcely be expected, therefore, that any other metal could directly replace
potassium. If such should happen, we would have an instance of rever-
sal, and should expect to find, on examination of the conditions, an agent
capable of doing just the reverse work of what is usually assigned to affinity.

It is also well known that in a simple voltaic cell, such as zinc con-
nected with platinum in dilute hydrochloric acid, the more powerful or
electro-positive metal zinc displaces the hydrogen that is in combination
with chlorine, and the hydrogen makes its appearance against the less
powerful or electro-negative metal platinum. The chemical theory of
galvanism supposes that the force originates in the chemical action which
takes place between the zinc and the acid; the contact theory supposes
that it originates in some unexplained manner in the opposite electrical
condition of the two metals induced by their contact. If the chemical
theory be the true one, it is evident that a zinc-platinum cell can only be-
come active when the binary liquid contains hydrogen or some metal
which is less powerful than zinc. If, for instance, we were to employ a
potassium salt instead of a hydrogen compound, it is inconceivable, on the
pure chemical theory, that there should be any action at all.

Such an action, however, does take place if we substitute an aqueous
solution of the chloride of potassium for the hydrochloric acid; the zinc
combines with the chlorine, and the potassium is set free in some form,
against the platinum, manifesting itself by the presence of free alkali and
hydrogen gas. The same holds good with aqueous solutions of chloride
of sodium or ammonium, or barium, strontium, calcium, or magnesium.

This action is slow; but if magnesium be used instead of zinc, it takes
place sufficiently rapidly to be easily observed, and we have therefore
studied the action of platinum and magnesium in connexion.

Experiments with Potassium Chloride.

The solution employed was neutral to test-paper, and contained 5 grms. of salt in 100 cub. centims. of water. A strip of magnesium connected with one of platinum was immersed in such a way that the two metals remained about ¾ inch apart. Bubbles of gas immediately made their appearance on the platinum; and a strip of red litmus-paper being placed in various parts of the solution, became strongly blue in the vicinity of the platinum plate, whereas but the faintest trace of alkaline reaction was observable near the magnesium plate; magnesium was found in solution.

A similar experiment was made in a cell which was divided in the middle by means of parchment-paper. The strip of platinum in one division was connected with the strip of magnesium in the other by means of a wire, and allowed to remain for an hour, when they were removed. The liquid in the division which had contained the magnesium was slightly turbid and faintly alkaline, but did not give the slightest precipitate when poured into a solution of magnesium sulphate. The liquid in the division that had contained the platinum plate was, on the contrary, clear and strongly alkaline; and it precipitated magnesium hydrate from the neutral solution of that metal. This conclusively showed the presence of some alkaline hydrate other than magnesium hydrate, and which could not have been any thing else than potassium hydrate. The liquid in the second division was about eight times as alkaline as that in the first.

We conceive that the explanation of this reaction is that the potassium chloride in solution is itself electrolyzed. The occurrence of hydrogen against the platinum plate might be ascribed to the electrolysis of the water, the resistance of which was diminished by the dissolved salt; but this alone in no way accounts for the simultaneous formation of free alkali. If any objector should contend that the nascent hydrogen had decomposed chloride of potassium, that would still leave the removal of the acid unexplained; and as the liberated potassium would instantly decompose an equivalent of water, we should have a chemical reaction resulting in nothing but the restoration of the original state of things,

$$H + KCl + H_2O = HCl + KHO + H = KCl + H_2O + H.$$

It might be supposed that the force produced by the contact of the two metals would expend itself upon the decomposition of a small amount of potassium salt, and that then the action would cease. But experiment shows the action just described to be continuous. Several determinations were made of the alkali in the divided-cell experiment described above, at 30 minutes' and at 60 minutes' duration. The results were far from uniform; but on the average the double period showed an increase of 70 per cent. Better observations were obtained when the hydrogen evolved was taken as the measure of the action. The wire connecting the strips of magnesium and platinum was caused to pass through the whole length of a graduated

tube, which was filled with the solution and inverted in it as in the annexed diagram.   Hydrogen was evolved at once, and a certain volume was col-

lected in 14 minutes ; a similar volume required 15 minutes, and so on, as in the subjoined Table.
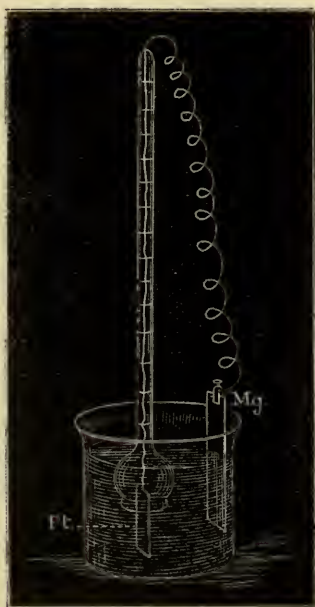
	Time required.
First measure..................	14 minutes.
Second ,, ...	15 ,,
Third ,, ...	16 m. 50 sec.
Fourth ,, ...	17 ,, 40 ,,
Fifth ,, ...	19 ,, 20 ,,
After 20 hours	25 minutes.

After some time a white precipitate formed, the product of the action of the potassium hydrate and magnesium chloride, which increased in amount.   The evolution of gas continued until the whole of the magnesium immersed had disappeared.

Sodium Chloride.

Similar experiments were made with a neutral solution of chloride of sodium containing 5 per cent. of salt.   Judging by one experiment with the divided-cell arrangement, the sodium salt was decomposed somewhat more quickly than the potassium salt, as might be anticipated.

Volta, in his original pile, employed a solution of common salt as the exciting liquid.   It seems to have been generally assumed, at least in late

years, that it is the water alone that is decomposed; but as a matter of fact the plates become alkaline.

Ammonium Chloride.

On employing a 5-per cent. solution of ammonium chloride, free ammonia and hydrogen were obtained at the platinum plate. On causing the platinum to dip into a little mercury during the reaction the mercury increased in bulk, owing to the formation of the so-called ammonium amalgam.

Chlorides of Metals of the Alkaline Earths.

The chlorides of barium, strontium, and calcium are easily decomposed by magnesium in connexion with platinum. The hydrates pass into the liquid until it is saturated, when they precipitate. Of course hydrogen escapes at the same time from the platinum plate.

Other Combinations.

As might be expected, these actions are not confined to chlorides. The sulphates and nitrates of potassium and sodium give similar results in the magnesium connected with platinum, an alkaline hydrate always appearing against the platinum plate.

If one metal in conjunction with another more electro-negative than itself will decompose the salt of a more positive metal in aqueous solution, it may be expected, *à fortiori*, that it can decompose one of its own salts. Instances of this are not wanting.

Magnesium connected with platinum will decompose a magnesium salt, the almost insoluble hydrate of magnesium being found adhering to the negative metal. The deposition of zinc on the plates of an old-fashioned battery, when the battery is pretty well exhausted, is a well-known phenomenon. In our experiments with copper and silver in conjunction in a solution of nitrate of copper, we never succeeded in reducing the galvanic action to *nil* by our utmost efforts to exclude all oxygen: and the whole of the present inquiry originated in an experiment described by us before the Physical Society, that mercury and gold in conjunction would decompose mercuric chloride with the deposition not only of the lower chloride, but also of metallic mercury upon the gold.

[We reserve for further consideration the part played by the water in these decompositions, and the bearing of the experiments on the rival theories of voltaic action.—Nov. 26.]

DECOMPOSITION OF WATER BY THE JOINT ACTION OF ALUMINIUM AND OF ALUMINIUM IODIDE, BROMIDE, OR CHLORIDE, INCLUDING INSTANCES OF REVERSE ACTION.

By J. H. GLADSTONE, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and ALFRED TRIBE, Esq., Lecturer on Chemistry in Dulwich College.

IN the course of our work with the copper-zinc couple, we described somewhat briefly a series of bodies which may be regarded as zinc ethylate in which chlorine, bromine, or iodine has taken the place of one C_2H_5O, and which may well be termed *zinc-halogen ethylates*. The non-crystalline character of these compounds, coupled with the difficulty of removing the alcohol with which they necessarily become associated, render their study difficult and after all unsatisfactory. We thought, however, that some knowledge of the reactions of bodies of this character might be obtained, could we succeed in replacing the zinc by some other metal. We therefore set to work in the hope of preparing an analogous aluminium compound, and in so doing observed a phenomenon which induced us to undertake the experiments detailed below. We give them much in the order in which they were made.

Experiment I.—2 grams of aluminium-foil 42 cm. long, 5 cm. wide, cut in small pieces, were placed in a flask with 20 c.c. of water and 7 grams of iodine. Evolution of gas, which proved to be hydrogen, took place at once at the ordinary temperature. The flask was kept in water at 12°, and the following measurements made :—

Collected in the first		15	minutes	....	650	c.c.
,, ,,	second	15	,,	....	1050	,,
,, ,,	third	15	,,	....	300	,,
,, ,,	next	40	,,	....	110	,,
					2110	,,

The residue in the flask was quite thick and extremely difficult to wash. It consisted of a little aluminium and the elements of aluminic oxide and iodide.

Experiment II.—Similar to experiment I, but only 2 grams of iodine were employed. There was a very slight action noticeable at the ordinary temperature. The flask was now heated by immersion in boiling water. In 15 minutes the whole of the iodine had disappeared, and there was

Collected in the first   30 minutes.......... 300 c.c.
  „   „   second 30   „   .... 400 „
  „   „   third   30   „   .... 250 „

The evolution continued in a diminishing ratio for 17 hours, the total gas obtained measuring 1915 c.c. The aluminium left in the flask weighed 0·284 gram.

Experiment III.—Similar to experiments I and II, a still smaller quantity of iodine (1·44 gram) being employed. At a temperature of 100°, in 15 minutes, the free iodine had disappeared and 80 c.c. of gas were collected. The experiment was continued for 23 hours, 1341 c.c. of gas being collected. One gram of aluminium was found in the residue.

These experiments differ only in the amounts of iodine employed; still it is evident that the hydrogen obtained bears no relation to this iodine, but is practically proportional to the amount of metal used up.

This suggested that the decomposition of water which obviously takes place was probably occasioned by a series of decompositions and recompositions of the aluminic iodide produced in the first instance by the direct union of its elements. Further evidence of this appeared desirable, and the following experiments were accordingly made.

Experiment IV.—2 grams of aluminium with 20 c.c. of aqueous hydriodic acid containing 2 grams of anhydrous HI were placed in a flask fitted with a delivery-tube. At the ordinary temperature there was no action in 15 minutes, but upon immersing the flask in boiling water, evolution of hydrogen took place immediately.

In the first   15 minutes .... 200 c.c. had collected.
  „ second 15   „   .... 190 „   „

And the evolution of gas proceeded in a diminishing ratio for 18 hours, when action practically ceased. There remained 0·352 gram of aluminium in the flask, showing that 1·648 grams had undergone oxidation during the experiment. This is equivalent to 2020 c.c. of hydrogen, while the amount actually obtained was 2004 c.c. The hydrogen in the 2 grams of acid employed amounted to only 175 c.c.. It is therefore evident that the greater part of the hydrogen must have come from the decomposition of water.

Experiment V.—As doubts may arise in the mind with regard to the part played by the iodine and hydriodic acid in the experiments already described, we instituted the following additional experiment:—3·8 grams of pure anhydrous aluminic iodide were mixed with 2 grams of finely cut aluminium foil and 20 c.c. of water were added, little by little, so as to prevent a rise of temperature from the combination of the iodide with water. The flask was heated to 100°. Hydrogen was at once evolved, measuring 200 c.c. in 15 minutes, and continued in a diminishing ratio for 6 hours, when ·065 of metallic aluminium was found in the flask, showing that 1·935 had been used up, a quantity equivalent to 2372 c.c. of gas. The actual amount obtained was 2187 c.c.

That water readily decomposes by the joint action of aluminium and its iodide is a fact well established by these experiments. But why this reaction ?

Water forms a definite crystalline hydrate with aluminic iodide (Weber, *Pogg. Ann.*, cvii, 264), and from our own observation we know that the iodide dissolves in water without apparent decomposition. According to Deville, we also know that aluminium decomposes water at a white heat only, and we have found that the metal employed by us could be boiled in water for hours without the production of a trace of hydrogen. Yet water undergoes rapid decomposition in presence of the two substances, either of which alone does not affect it.

Two explanations have presented themselves.

First. That the aluminium undergoes direct oxidation at the expense of the water, in consequence of the disturbing influence of the iodide—

$$2Al + Al_2I_6 + 3H_2O = Al_2O_3 + Al_2I_6 + 6H,$$

that is to say, the iodide undergoes no change.

Second. That the aluminium of the iodide is oxidized and the iodide regenerated, which may thus be brought about—

$$Al_2I_6 + 3H_2O = Al_2O_3 + 6HI$$
$$6HI + 2Al = Al_2I_6 + 6H,$$
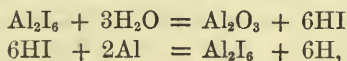
and so on, which may be supposed to take place through the intervention of oxyiodides.

It is well known that hydrated haloid aluminium salts split up by heat and give off free acid. We endeavoured to find some direct evidence of the presence of free acid in solutions such as we used in our experiments, but without conclusive result, although we found that a small quantity of hydrobromic acid was given off from a saturated solution of the hydrated aluminic bromide (containing excess of the crystalline hydrate) when heated to 100° C.

Either view accounts for the facts, but which is the truer we at pre-

sent see no means of determining, although the latter seems to us more probable.

We thought, it would be of considerable interest to determine whether other metals or other compounds could be substituted for aluminium and its iodide.

Neither zinc nor iron, heated with their respective iodides in water, yielded any hydrogen; but both zinc and iron, when heated with aqueous aluminic iodide, occasion the decomposition of water.

Experiment VI.—6·5 grams of zinc foil cut in small pieces were heated at 100° C. with 10·69 grams of aluminic iodide (slightly basic) and water.

In the first 15 minutes ...... 100 c.c. hydrogen were collected.
  ,,   second 15 ,, ... 40 ,,   ,,   ,,
  ,,   third 15   ,, ... 14 ,,   ,,   ,,

The action was continued for 49 hours when the evolution of gas had almost ceased. The total measured 681 c.c. The aluminic iodide taken is equivalent to 880 c.c. In the flask there was noticeable a white powder, which proved to consist mainly of aluminic oxide with a very little zinc oxide. The liquid consisted principally of a solution of zinc iodide with a little aluminic iodide or oxide. The zinc remaining was also found to be studded here and there with crystalline metallic plates, presumably metallic aluminium.

It is evident, from the results of this experiment, that zinc replaces aluminium from its iodide in aqueous solution, and this gives at once the elements of the original reaction.

The action may be represented thus :—

$$Al_2I_6 + 3Zn = 3ZnI_2 + Al_2$$
$$Al_2 + Al_2I_6 + 3H_2O = Al_2O_3 + Al_2I_6 + 6H.$$
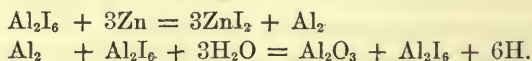
Experiment VII.—The action with iron is extremely slow. 8 grams of iron in fine wire were heated to 100° with the same quantity of Al_2I_6 solution as in the last experiment. In 41 hours 493 c.c. of hydrogen had collected, when its evolution practically ceased. Ferrous and aluminic iodide were found in solution, and either aluminium, or more probably its oxide, adhering to the iron.

Experiment VI has shown that zinc replaces aluminium from its iodide when in solution. It now occurred to us to ascertain whether the reverse action was possible (*i.e.*, whether zinc could be replaced by aluminium).

Experiment VIII.—9·9 grams of iodine, equivalent to the amount of Al_2I_6 employed in experiment VI, were heated with an excess of pure zinc and 20 c.c. of water until the solution was perfectly colourless. After removing the undissolved zinc, 2 grams of aluminium were

added and the whole heated by immersion in water at 100°. No signs of action were apparent for 15 minutes, when gas began to be evolved, and this continued at an increasing rate for 3 hours, after which it slowly declined, until in 15 hours 1538 c.c. had collected. The residue in the flask was of a thick pasty consistency, from which water dissolved zinc iodide and a little aluminic iodide or oxide. The portion insoluble in water consisted principally of aluminic oxide with some zinc, probably as oxyiodide. This experiment was repeated several times with different quantities of zinc iodide with practically the same result.

An experiment similar to the last was made, an equivalent amount of ferrous iodide being employed. Action commenced at once upon heating to 100°, and the aluminium-foil became quickly coated with a black substance which was found to be metallic iron. The hydrogen collected during 16 hours measured 1917 c.c. As in previous experiments, the residue in the flask was very pasty. Water dissolved from it a little ferrous iodide and some aluminic iodide, the portion insoluble being principally aluminic oxide and metallic iron.

The evolution of hydrogen in the two experiments just described is in all probability to be attributed to the replacement of zinc and iron by aluminium and the formation of aluminic iodide, which, in presence of aluminium, would give the original reaction; thus:—

$$3FeI_2 + Al_2 = 3Fe + Al_2I_6$$
$$Al_2I_6 + 3H_2O + Al_2 = Al_2O_3 + Al_2I_6 + 6H.$$
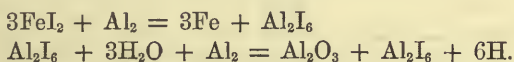
Of course some of the hydrogen in the ferrous experiment might (since iron was actually found) have been due to the action of an aluminium-iron couple upon the water present. Whether this be so or not, it is certain that iron and zinc can replace aluminium, which, in its turn, by slightly altering the conditions, can replace both zinc and iron. It is possible that this may take place through the intervention of oxy-salts in solution; thus the action of water on zinc iodide, for example, may be the production more or less of such a compound as

$Zn_2OI_2.2HI.$ or $\left\{ \begin{array}{l} ZnHI_2 \\ O \\ ZnHI_2 \end{array} \right.$, the hydriodic element of which would yield
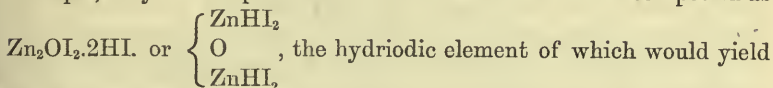
up its hydrogen under the action of the aluminium, and this would of course give all the elements of the original reaction.

It now appeared to us of interest to ascertain whether the bromide or chloride could take the place of the iodide in the original reaction. Experiments were accordingly made.

Experiment IX.—Similar to experiment VI, an equivalent quantity, 2·49 grams, of aluminic bromide being employed. At 100° evolution of hydrogen commenced at once.

During the first 15 minutes .... 120 c.c. were collected.
       ,,   next 45   ,, ... 750 ,,   ,,

The action continued in a diminishing ratio for 6 hours, when it was found that 2378 c.c. of gas had been given off. Aluminic oxide and bromide, with a very little aluminium remained in the flask.

Experiment X.—Similar to experiment IX, an equivalent quantity, 1·24 grams, of aluminic chloride being employed.

In first 15 minutes......   50 c.c. of gas were given off.
In first hour .... 1770 ,,   ,,   ,,

The action continued in a rapidly diminishing ratio for about six hours, when a total of 2345 c.c. of gas had been reached. The residue in the flask was similar to that of the previous experiment.

It is evident from this that both the bromide and chloride of aluminium act much in the same manner as the iodide.

A comparison of results, as seen in the subjoined table, is of interest :—

Time.	Equivalent quantities of		
	Al_2I_6.	Al_2Br_6.	Al_2Cl_6.
15 minutes	200 c.c of H	120 c.c.	50 c.c.
60 ,, ...	550 ,,	870 ,,	1770 ,,
6 hours	2187 ,,	2378 ,,	2345 ,,

The same quantity of aluminium, viz., 2 grams, was employed in all the experiments. This is theoretically equivalent to 2453 c.c. of hydrogen. It should be mentioned that the aluminic haloïd salts were purposely made slightly basic.

Apart from the theoretical interest attaching to the experiments detailed above, we have reason for believing that the reactions described are of value, as they may afford the means of hydrogenizing in neutral solution compounds on which the copper-zinc couple has no influence.

NOTES ON THE ACTION

OF

THE COPPER-ZINC COUPLE.

BY

PROFESSOR GLADSTONE

AND

ALFRED TRIBE*.

Relative Activity of pure Zinc and Zinc covered with spongy Copper.

A SOLUTION of sulphuric acid containing $3\frac{1}{2}$ parts of acid to 1000 of water is just acted upon by pure zinc.

In an experiment with 2·5 grms. pure zinc (granulated) immersed in this strength of acid, 7 volumes of hydrogen were given off in one hour.

In another experiment, in which the same piece of zinc upon which ·003 grm. of copper had been deposited was used, 80 volumes of hydrogen were given off in the same time.

Thus it appears that the activity of zinc in very dilute sulphuric acid is increased elevenfold by 0·12 per cent. of the negative metal.

Arseniuretted Hydrogen.

If zinc containing arsenic act upon dilute sulphuric acid, the hydrogen, as is well known, contains AsH_3, the formation of which is explicable (from analogy with what is known of the action of hydrogen upon oxynitrogen compounds) on the supposition that the arsenic becomes dissolved, and that by the subsequent action of hydrogen upon the arsenical compound in solution the arseniuretted hydrogen is produced.

Some four years ago we pointed out that the copper-zinc couple

* Read before the British Association at Bristol, August 1875.

in presence of water effects the decomposition of that fluid—zinc-hydrate and hydrogen being produced.

According to Bonsdorff, arsenic does not dissolve in water free from dissolved oxygen—a fact which we have verified, and also that dilute sulphuric acid does dissolve it.

If the foregoing view of the formation of AsH_3 be correct, the hydrogen obtained by the action of the couple upon water should be free from arsenical gas, even though the couple be made with arsenical zinc.

We give the results of four experiments.   A quantity of arsenical zinc-foil was "coupled" with copper, washed, and heated with water; and two litres of gas evolved were passed through a tube heated to redness.   Not a trace of arsenic was noticeable.

A portion of the same foil not "coupled" was treated with dilute sulphuric acid, and two litres of hydrogen evolved by the action were passed through a tube heated as before.   0·0019 grm. of arsenic was deposited in the cool part of the tube.

The arsenical zinc with a covering of spongy copper, when treated with dilute sulphuric acid, gave arseniuretted hydrogen, which appears to point to the conclusion that it is not the copper, but the inability of the arsenic to get into solution, that accounts for the absence of hydrogen in the gas from water and the couple—a conclusion that was confirmed by adding a dilute solution of arsenic (1 part $As_2 O_3$ in 12,000 of water) to some couple, when immediately the arsenical mirror was produced in the heated tube.

THE AUGMENTATION

OF THE

CHEMICAL ACTIVITY OF ALUMINIUM

BY

CONTACT WITH A MORE NEGATIVE METAL.

BY

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HAVING had occasion to employ aluminium for effecting certain decompositions, we were induced to determine whether covering its surface with more-negative metals would so augment its chemical activity as to enable it to decompose water below or at 100° C.

According to Deville, the metal *alone* does not decompose water except at a white heat.

The following experiments were made.

(*a*) 0·43 grm. of metallic copper was deposited upon 6 grms. of aluminium-foil (126 centims. long, 5 centims. wide) in a two-ounce flask by immersion in very dilute copper-sulphate solution very slightly acidulated with hydrochloric acid. The couple so obtained was completely freed from sulphate and chloride by washing with pure water.

(*b*) 0·2214 grm. of platinum was deposited upon a similar quantity of aluminium-foil by immersion in dilute platinic chloride and was washed as in the former instance.

The flasks containing these preparations were filled with water and allowed to stand at the temperature of the air for twenty-two hours, when they were heated to 100° C. Hydrogen gas was evolved.

The results obtained were as follows :—

* Read before the British Association at Bristol, August 1875.

Temperature.	Time.	Al-Cu experiment. Hydrogen.	Al-Pt experiment. Hydrogen.
$1\overset{\circ}{2}$ C.	22 hours	cub. centim. 2·5	cub. centim. 4
100	next 6 ,,	375	484
,,	,, ,,	92	114
,,	,, ,,	55	78
,,	,, ,,	33	45

The action proceeded, at a diminishing rate, for several days.

The fact brought out by the above experiments was further established by other decompositions, and is of course corroborative of our work with zinc conjoined to more negative metals in a spongy condition.

THE DECOMPOSITION OF ALCOHOL AND ITS HOMO-LOGUES BY THE JOINT ACTION OF ALUMINIUM AND ITS HALOGEN COMPOUNDS.

By J. H. Gladstone, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and Alfred Tribe, F.C.S., Lecturer on Chemistry in Dulwich College.

In our paper on the joint action of aluminium and the aluminium-halogens on water, the fact, among others, was established that water is decomposed by these agents, the hydrogen obtained being equivalent to the metal employed.

The exact products resulting from the decomposition of water may be known *à priori;* but with regard to any complex organic body it is very different. Alcohol, for example, if it should be decomposed when subjected to the action of aluminium and its iodide, might be expected to yield either ethyl hydride and aluminic oxide, or hydrogen and aluminic ethylate. If the former, the reaction would give an easy means of obtaining the hydrides of the alcohol-radicals; if the latter, it would add another member to an important class of organo-metallic bodies, and possibly supply the means of hydrogenising many organic substances soluble in alcohol, without the destructive action of acids or alkalis. These considerations induced us to undertake the study of the action of aluminium jointly with its halogens on alcohol and its homologues.

Alcohol was found to have no effect on aluminium alone, even when boiled with it for some hours.

2 grams of iodine were dissolved in 20 c.c. of absolute alcohol, and placed in a flask containing 2 grams of finely-cut aluminium foil. Action commenced immediately, the temperature inside the flask rising so rapidly as to necessitate agitation in cold water. In the course of three minutes the colour of the iodine had entirely disappeared.

In 2 minutes........	350 c.c. gas were collected.	
Next 1 minute	650 ,,	,,
,, 4 minutes......	1000 ,,	,,
,, 3 ,, ...	100 ,,	,,

The residue in the flask being now quite solid, 20 c.c. more alcohol were added, when gas was again evolved. In 17 minutes from the commencement the action ceased, 2184 c.c. of gas having been obtained.

In another experiment, the same quantity of materials was employed as in the previous trial, the flask with its contents being from the beginning immersed in water at 17° C. In two minutes evolution of gas commenced, and the free iodine disappeared in 39 minutes.

$$
\begin{array}{lll}
\text{Gas collected during first hour} \dots . & 310 \text{ c.c.} \\
\qquad ,, \qquad ,, \quad \text{next } \tfrac{1}{2} \text{ hour} \, .. & 430 \text{ ,,} \\
\qquad ,, \qquad ,, \quad ,, \quad 3 \text{ hours} .. & 1360 \text{ ,,}
\end{array}
$$

Evolution continued slowly for 15 hours longer, the total gas collected measuring 2165 c.c.

The gas obtained gave complete contraction on explosion with oxygen, and burnt with a non-luminous flame, the only product of combustion being water, showing that the gaseous product of the action is hydrogen.

The quantity of hydrogen equivalent to 2 grams of aluminium, minus the quantity necessary to combine with 2 grams of iodine, is 2277 c.c. It is evident, therefore, that hydrogen is obtained equivalent to the metal used up not in combination with iodine.

Our object in employing free iodine in the experiments just described was simply because it offered the most direct and ready means of preparing a known quantity of aluminium iodide. We, however, thought it of importance to make the following experiment, with the view of ascertaining whether free iodine was necessary to start the reaction.

2·2 grams of aluminic iodide (equivalent to 2 grams of iodine) were dissolved in 40 c.c. absolute alcohol, and added to 2 grams of cut aluminium foil, the temperature being 17° C. Evolution of gas commenced in 35 minutes.

$$
\begin{array}{lll}
\text{Collected in following 90 min.} \dots \dots & 430 \text{ c.c.} \\
\qquad ,, \qquad ,, \quad 30 \text{ ,,} \dots \dots & 570 \text{ ,,} \\
\qquad ,, \qquad ,, \quad 15 \text{ ,,} \dots \dots & 1530 \text{ ,,}
\end{array}
$$

when action practically ceased. The temperature rose considerably during the reaction. The total gas collected, after allowing for temperature, &c., measured 2381 c.c., the quantity theoretically obtainable from the aluminium employed being 2452 c.c.

It is evident from the results of this experiment that alcohol suffers decomposition by the joint action of aluminium and its iodide; and on comparing it with Experiment I, it is noticeable that the reaction is considerably increased in rapidity by the iodine being free, which is doubtless to be attributed to the greater disturbing influence exercised on the alcohol by the element when free than when in combination.

The residue left in the flask was pasty and greyish white in colour;

and as hydrogen is the only gaseous product of the reaction, it is hard to conceive of it consisting of other than aluminic ethylate, $Al_2(C_2H_5O)_6$, mixed with about one-thirteenth of an equivalent of aluminic iodide, or of one-sixth of an equivalent of aluminic iodo-ethylate, $Al_2 \left\{ \begin{array}{l} C_2H_5O)_3 \\ I_3. \end{array} \right.$

Heated to 100° C. it dried up, so that it could be easily powdered, a quantity of alcohol having distilled. On further heating in a paraffin bath to 275° C. it became fluid at about 180°, alcohol mixed with an oily body containing iodine, and having the odour of ethyl iodide, passing over during the whole time. After keeping the fused residue at 275° C. until nothing more distilled, 2·407 grams were removed, and the aluminium and iodine were determined. ·4388 aluminium and ·03152 iodine were obtained. Now, since iodine and aluminium were originally together in equal quantities, it is evident that the 2·407 grams of residue must have lost ·4072 of iodine; and as this appeared in combination with ethyl, there can be little doubt that it resulted from the decomposition of aluminic iodo-ethylate, thus :—

$$Al_2 \left\{ \begin{array}{l} (C_2H_5O)_3 \\ I_3 \end{array} \right. = Al_2O_3 + 3 \left\{ \begin{array}{l} C_2H_5 \\ I \end{array} \right.,$$
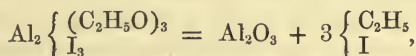
which would of course add to the residue a quantity of aluminic oxide equivalent to the iodo-ethylate decomposed. Calculating the composition of the 2·407 grams of residue from its analysis on this hypothesis, we have :—

Aluminic ethylate equivalent to the aluminium found, minus the metal in the under-mentioned

Al_2O_3 and $Al_2 \left\{ \begin{array}{l} (C_2H_5O)_3 \\ I_3 \end{array} \right.$	2·2273
Iodo-ethylate equiv. to iodine found	0·0472
Alumina equiv. to iodine lost..	0·1097
	2·3842

The close agreement of these numbers leaves little doubt as to the composition of the solid products of the reaction, and we have other grounds for believing in the existence of the aluminic iodo-ethylate and its decomposition according to the above formulæ. These grounds we hope to set forth in a future communication.

Aluminic Ethylate.

The residue, heated above 275° by means of a gas flame, boiled, and at the same time underwent a partial decomposition; a small amount of a yellowish-white substance containing aluminium condensed in the

tube of the condenser; a little liquid containing alcohol and some
aluminium compound decomposible by water was found in the receiver;
some quantity of gas was collected which contained 86·4 p. c. of an
olefine; while in the flask after the action, was found alumina and a
mere trace of iodide.   The following equation represents the probable
action of heat on such a body as aluminic ethylate:—

$$Al_2(C_2H_5O)_6 = Al_2O_3 + 3C_2H_5HO + 3C_2H_4,$$
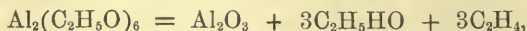
which is in accordance with what we obtain by the action of heat on
our solid residue.

The foregoing results led us to hope that the ethylate might be ob-
tained in the pure state by distillation under diminished pressure.
The residue from the usual quantities of 2 grams of aluminium,
2 grams iodine, and 40 c.c. alcohol, after heating for some time at
about 270° C., was gently heated over a gas lamp, a pump connected with
the condenser tube being kept at work.   A quantity of vapour passed
over which immediately condensed in the tube to a yellowish-white
solid.   The alumina left in the flask weighed only 0·372 gram, which
shows that 90 p. c. of the metal taken passed over in combination.   The
solid body thus distilled was found to be quite free from iodine.   It
dissolved slightly in absolute alcohol, from which solution water pre-
cipitated aluminic hydrate.   Hot water decomposes it very rapidly,
alcohol and aluminic hydrate being the products of decomposition.   It
melts at 115° C., and boils somewhere about the limits of the mercu-
rial thermometer.   Exposed to the ordinary air it quickly decomposes,
alumina and doubtless alcohol being produced.

1·062 gram dissolved in dilute nitric acid and precipitated by
ammonia gave 0·330 Al_2O_3; the calculated quantity for aluminic ethy-
late being 0·336.

In this aluminic ethylate, the existence of which we may now con-
sider well established, we have the second instance of an organo-
metallic body containing oxygen capable of distillation, cacodylic
oxide having been the first recorded.

It now appeared of interest to ascertain whether in this reaction
ethyl alcohol could be replaced by other alcohols of the same series,
and whether the iodide could be replaced by its chlorine or bromine
analogue.

Aluminium and aluminic iodide boiled with methyl alcohol for two
hours gave no result, but on replacing the methylic by amylic alcohol,
action took place, the course of which is shown by the following
experiment:—

2·14 grams of aluminic iodide were dissolved in 40 c.c. of amyl

alcohol, and the mixture added to 2 grams of finely cut aluminium foil. No gas was evolved, or any signs of action in 15 minutes at the ordinary temperature; at 100° C. evolution of gas commenced in 8 minutes, and the action became so rapid as to necessitate the agitation of the flask in cold water. In 10 minutes 1,500 c.c. of gas were collected, and in 25 minutes more the action ceased, the total hydrogen obtained measuring 2,272 c.c., a quantity practically identical with what was obtained in the experiments with ethyl alcohol.

Alcohol boiled with aluminic chloride and the metal for two hours underwent no decomposition. The bromide, however, was found to bring about its decomposition, but less energetically than the iodide, as the following experiment illustrates :—

1·44 gram of aluminic bromide (equivalent to the iodide employed previously) was dissolved in 40 c.c. absolute alcohol, and added to the usual amount of cut aluminium foil. In 12 minutes evolution of gas commenced, and in the next 60 minutes 160 c.c. had collected; in the next 38 minutes 840 c.c. more, and this continued in a diminishing ratio for five hours, the total hydrogen obtained measuring 2,275 c.c., which is again nearly equivalent to the quantity of aluminic ethylate which it is theoretically possible to obtain.

The reaction just described appears to us to be remarkable in more respects than one. We have here a powerful agent for separating oxygen and oxy-radicals from their compounds; and we have the peculiar fact revealed that a body so stable as alcohol is easily split up by the conjoint action of two substances, neither of which singly and under the same conditions has the least action upon it.
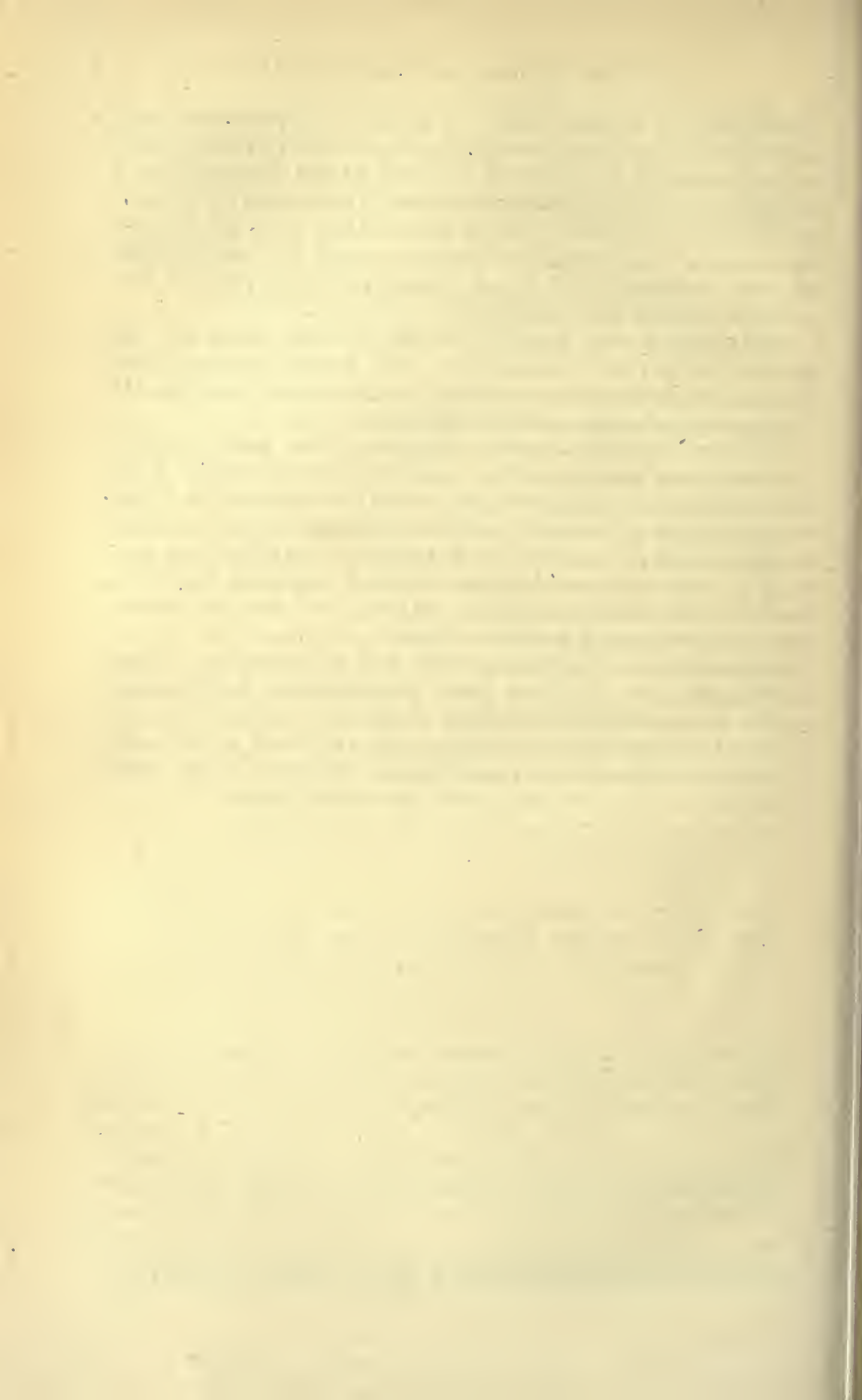
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PROFESSOR J. H. GLADSTONE, Ph.D. F.R.S.

Methods of Chemical Decomposition as illustrated by Water.

AMONG the most venerable of the Chinese classics is the 'Shoo King,'
a collection of ancient historical records; and one of these records, the
fourth book of Chow, contains a still more ancient document, "The
Great Plan with its nine divisions," which purports to date from
the early part of the Han dynasty,—according to Dr. Legge about
2000 B.C. This remarkable treatise bears on physical as well as
ethical philosophy, and commences with an account of the five ele-
ments, viz. water, fire, wood, metal, and earth. The first element,
water, is said to "soak and descend," and also to "become salt."

This seems to be the earliest known record of that doctrine of
elements which spread widely over the ancient world. In the
'Institutes of Manu' we read of the elements also as five, but they
are earth, fire, water, air, and ether; and according to the cosmogony
of the Hindoo legislator, light or fire produced water, and water
produced earth. There was, however, at least as late as two centuries
ago, a sect in India who held it as a religious tenet that water was
the prime or original element.

Similar opinions found their way to Europe. Thus Thales, of
Miletus, who flourished in the sixth century B.C., taught that water was
the origin of all things. The Greek philosophers generally adopted
the theory of several elements, but reduced the number to four,—fire,
air, earth, and water.

It is hard to say what was the precise meaning attached by the
ancients to the term "element." It no doubt did not always convey
the same idea. Water also, at least in the Aristotelian philosophy,
was a generic expression for many bodies in a fluid condition, and sig-
nified not so much a special material substance as an inherent quality
of things. Thus it was said to be cold and moist, and the opposite of
fire which was hot and dry. In the philosophy of the middle ages we
find the same views prevailing, and the early chemists still looked

upon water in the same light. Thus Becker enumerated five elements, air, water, and inflammable, mercurial, and infusible earth; while Stahl adopted four,—water, acid, earth, and phlogiston. The ancient theory maintained its hold till the experimental philosophers at the latter part of the eighteenth century gave a definite meaning to the term element, and showed that water, air, and earth are compound bodies. Yet the idea of the elementary character of water was not easily abandoned.

In 1781 Cavendish found that when a mixture of what were then called " inflammable air " and " dephlogisticated air " is exploded by a spark in such proportions that the burnt air is almost entirely phlogisticated, pure water condenses on the sides of the vessel, and is equal in weight to the weight of the two airs. His theory was that water consists of " dephlogisticated air united to phlogiston," and that " inflammable air is water united to phlogiston." At the time of explosion, according to him, the excess of phlogiston was transferred from the inflammable to the dephlogisticated air, and thus both airs " turned into water." Cavendish also explained Priestley's production of inflammable air on heating iron filings strongly, by contending that the phlogiston of the iron united with the moisture from which they had not been freed. Lavoisier gave a different explanation of these phenomena. He held that "dephlogisticated air" is an elementary substance—oxygen—united with imponderable caloric, and that " inflammable " air, or hydrogen, is capable of taking the oxygen from the caloric, thus producing water and heat. " Water is not a simple substance, but is composed, weight for weight, of inflammable and vital air." Thus water was at length déposed from its rank as an element.

In the first year of this century, when the news of Volta's great discovery of the pile was made known in England, Messrs. Nicholson and Carlisle made various experiments with a series of halfcrowns, zinc plates, and pasteboard soaked in salt. Knowing that water conducted electricity, they inserted brass wires through corks at the two ends of a tube filled with water, which they are careful to tell us came from the New River. They were surprised to see a stream of minute bubbles rising from one pole while the other was corroded, and that this decomposition took place at each pole, though they were nearly 2 inches apart. They enlarged the distance, and found that 36 inches of water was too much for their force to traverse. Substituting flattened platinum for their brass wires, they found that the water was decomposed with the production of hydrogen at one end and oxygen at the other.

The old notion that water, by continuous boiling, was turned into stone had been previously dispelled by Lavoisier, but Davy found that some salts and earths remained behind when water was electrolyzed, and that when the experiment was conducted in two cells communicating with one another, the liquid in the one cell became acid, and in the other alkaline. He traced the origin of this in a masterly re-

search, which formed the Bakerian lecture for 1806.*   He found that
the earthy substances were original impurities in the water, or came
from the vessels employed; and using gold cones filled with distilled
water, and united together by asbestos, he convinced himself that
nitric acid was produced at the positive pole and ammonia at the
negative.   Suspecting that these were produced from the small quan-
tities of nitrogen dissolved in the water combining with the liberated
oxygen and hydrogen respectively, he took extraordinary precautions.
Making use of water which he had carefully distilled in a silver still
at 140° Fahr., and performing the experiment in vacuo, or rather in a
space which he had twice filled with hydrogen and exhausted as
thoroughly as the means at his disposal would permit, he then found
that the water was decomposed without the least production of either
acid or alkali.   " It seems evident then," wrote Davy, " that water,
chemically pure, is decomposed by electricity into gaseous matter
alone, into oxygene and hydrogene."

In the following year Davy discovered the metals of the alkaline
earths, potassium and sodium, and found that when these bodies are
thrown upon water they decompose it, appropriating its oxygen and
setting free its hydrogen.   This is due to the superior chemical
power or "affinity" of the alkaline metals.

In 1846 Mr., now Sir William, Grove observed that when steam
was subjected to something like a white heat, small quantities of mixed
oxygen and hydrogen gas were always produced.†   It has since been
shown that the gases are actually dissociated in one part of the flame
of the oxy-hydrogen blowpipe, after their first combination.

It thus appears that there are three distinct ways in which water
may be decomposed:—By an electric current;‡ by some substance
which has a superior attraction for one of its elements; or by heat
alone.

It will readily be understood that the power of any one of these
agents will be augmented by the co-operation of either of the others.
Thus, the action of chemical affinity is usually augmented by heat;
for instance, if a pellet of sodium be thrown upon cold water it melts,
on account of the chemical action at once set up, but if upon boiling
water it not only melts, but bursts into flame through the greater
violence of the action.   This is the reason why in Priestley's experi-
ment iron at a red heat decomposed steam, though it will not do so at
ordinary temperatures.

Similarly the electrolysis of water is much facilitated if there is
some chemical affinity between the oxygen and the metallic conductors.
It is generally said that it requires two cells to decompose water

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* 'Phil. Trans.' 1807, p. 1.

† *Ibid.* 1847, p. 1.

‡ Though voltaic electricity alone is referred to in this discourse, it is well
known that other forms of the same agent will effect chemical decompositions.
Thus Professor Andrews has resolved pure water into its constituent gases by
frictional electricity, and by that derived from the atmosphere.

electrolytically. Now it is true that if platinum poles are employed there is no visible disengagement of gas when one cell only is used; but with zinc poles a single cell of Bunsen or Grove is amply sufficient. Zinc alone without the voltaic current is incapable of displacing the hydrogen in water; but it must be borne in mind that the tendency to combine with oxygen is a constant property of this metal, and is easily brought into activity by the co-operation of the feeble voltaic current. The increased effect upon electrolysis which is due to the nature of the poles is in proportion to the electromotive force of the different metals. For pure water the order is,—zinc, lead, iron, copper, silver, platinum, as tested by a galvanometer. This difference of result according to the nature of the metals employed in the electrolytic cell appears generally to have been overlooked, and it is the feeblest metal—platinum—which is usually employed for experimental purposes, doubtless because it is incapable of oxidation—the very reason of its feebleness.

When the other metals of the above list are used, not only does the positive pole oxidize, but the oxide, or rather hydrate, dissolves more or less in the pure water, and becomes itself an electrolyte. The consequence of this is that the positive electrode gradually wears away, while the metal is transferred to the negative electrode, and is deposited upon it in crystalline fringes or filaments. With silver these are particularly beautiful, as they assume arborescent forms, especially when able to spread over the surface of the containing vessel.

The temperature also of the liquid subjected to electrolysis has a great influence upon the result. Thus in an experiment where zinc poles and pure water were employed, the deflection of a galvanometer was found to increase about fourfold between 5° C. and 80° C., and the action augmented nearly *pari passu* with the temperature.

A similar result occurs, as might be expected, when two dissimilar metals, such as zinc and copper, are placed in cold water in connection with one another, and the water is heated. The deflection was found to double between about 30° and 80° C., but the difference for every 5° at the higher temperatures was several times greater than at the lower ones.

Another very important point in the electrolysis of water is to reduce to a minimum the very great resistance offered by the water itself. This is effected by bringing the electrodes as near to one another as possible : and for the same reason, if the force be generated by the action of two dissimilar metals upon water, they should be brought into the closest proximity.

A still more powerful means of decomposing water would evidently be a combination, not of two, but of all three agents, chemical affinity, heat, and voltaic force acting at an insensible distance. Thus zinc has a strong affinity for oxygen, but is unable of itself to displace the hydrogen of water : when united, however, with a more negative metal, such as copper, its power is enhanced to such a degree that a

separation of the constituents does take place; but in the ordinary arrangement of a voltaic cell the action is so slight that no evolution of gas is perceptible. To produce a visible effect, the metals must not only be close together, but ought to touch one another at a myriad of points. This may be brought about by depositing the copper upon the zinc in a spongy condition; then the zinc will be oxidized, and bubbles of hydrogen will appear amongst the branches of the copper, even at the ordinary temperature, but the effect is greatly increased by the application of heat.

The arrangement just described is the "Copper Zinc Couple," which has been employed by Mr. Tribe and the speaker, and more recently by others, to effect a variety of chemical decompositions. Zinc foil is immersed in a solution of sulphate of copper until a black velvety deposit of the metal is produced; the soluble salts are then washed away, and the couple after being dried is ready to be placed in any liquid it is desired to decompose. Water was the first body experimented upon, and it was found that the action would go on as long as there was any metallic zinc left in union with the copper, the amount of hydrogen evolved gradually diminishing, though varying somewhat with the temperature of the day. The great influence exerted by heat is, however, better shown in the subjoined table, which gives the results of an experiment reduced to the unit of an hour's work.

At 2·2° C.	..	..	1·1 c.c. of hydrogen produced.
22·2	..	..	5·5 ,,
34·4	..	..	13·9 ,,
55·0	..	..	62·0 ,,
74·4	..	..	174·6 ,,
93·0	..	..	528·0 ,,

These figures strikingly exhibit the rapid acceleration of the action at the higher temperatures.

A greater effect may be produced by substituting for the copper a still more negative metal. Thus a zinc platinum couple acts with much greater energy upon water. Gold zinc couples, and many others also, have been tried, but gold has the practical disadvantage that the precipitated metal does not adhere well to the zinc. Aluminium alone does not decompose water, not even, according to Deville, at a red heat; but an aluminium copper couple decomposes it slowly, and an aluminium platinum couple more rapidly, even in the cold. One of the most recent discoveries is that aluminium when amalgamated with mercury is converted into hydrate even by the moisture of the air. The most powerful combination, however, might be expected to be that of the most positive and the most negative metal which can be conveniently brought together. These are magnesium and platinum; and in fact, if strips of magnesium foil be coated with finely divided platinum by immersing them in platinic chloride, and the resulting salts be washed away, a couple may be

obtained which produces a most vigorous evolution of hydrogen when it is placed even in cold water.*

The decomposition of water by the copper zinc couple was of course a matter of little practical importance; it does, however, yield hydrogen in a state of purity, even though the zinc be largely contaminated with such a substance as arsenic—a fact which may prove of great consequence in medico-legal inquiries. These observations on water led to a long series of experiments on other bodies, especially organic compounds. The action of the two metals in conjunction frequently effects not only the splitting up of a compound, but a redistribution of its elements; and this has resulted not only in the discovery of a simple means of producing various substances previously known, but the formation of several others hitherto unknown. Thus the first trials were made on iodide of ethyl in the hope that Professor Frankland's beautiful process for making zinc ethyl might be simplified; and not only was a better result obtained in a shorter time, but when the experiment was performed in the presence of alcohol it was found that pure hydride of ethyl was given off, and a new substance, the iodoethylate of zinc, remained in the flask.

Among the bodies which may be prepared more easily or in greater purity by the copper zinc couple are the following:

Hydrogen.	Olefiant gas.	Diallyl.
Methyl hydride.	Acetylene.	Zinc ethiodide.
Ethyl hydride.	Propylene.	Zinc ethyl.
Propyl hydride.	Diamyl.	Zinc amyl.
Amyl hydride.		

The substances that have been discovered by this agency are the following:

Zinc propiodide	.. ..	$Zn(C_3H_7)I.$
„ propyl	.. ..	$Zn(C_3H_7)_2.$
„ isopropyl ..	.. ..	$Zu(C_3H_7)_2.$
„ ethylobromide ..	.. ..	$Zn(C_2H_5)Br.$
„ iodoethylate	.. ..	$Zn(C_2H_5O)I.$
„ bromethylate	.. ..	$Zn(C_2H_5O)Br.$
„ chlorethylate	.. ..	$Zn(C_2H_5O)Cl.$

Zinc propyl is a volatile liquid body, of specific gravity $1 \cdot 098$, which takes fire spontaneously in the air, burning with a bluish-white flame. The haloid ethylates are a new class of bodies which have been prepared from both ethyl iodide and iodoform, and their corresponding bromine and chlorine compounds.

The couple has also thrown some light upon the chemical struc-

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* Phenomena resulting from different metals in combination have frequently been observed by several experimenters, and some of them are described by Mr. W. N. Hartley in the 'Chemical News,' vol. xiv. p. 73; but it does not appear that the metals have ever been freed from concomitant salts, or their action understood or appreciated.

ture of some of these organic bodies, as, for instance, by its different behaviour with the two isomeric bodies, chloride of ethylene and chloride of ethylidine. This is a direction in which future investigation is likely to be rewarded.*

This method of quietly bringing about a chemical change has found a practical application in the hands of Professor Thorpe for determining the amount of nitrates in samples of water, a question of great importance which has hitherto been also one of great difficulty. The nitric acid is reduced by the couple to the condition of ammonia. In a similar way chlorates are reduced to chlorides.†

The progress of research by means of the copper zinc couple was interrupted by the discovery of a curious reaction, by which also water and other substances may be decomposed. Metallic aluminium does not attack water by itself, neither does iodine; but if the three are brought into contact, oxide of aluminium is formed and hydrogen gas is evolved; and not only this, but the solution so produced will cause the oxidation of any excess of aluminium with the formation of an equivalent amount of hydrogen. It is not even necessary that free iodine should be employed, for iodide of aluminium itself will determine the oxidation of any amount of metal. This action is greatly quickened by coupling platinum with the aluminium. By employing alcohol instead of water, a similar action is set up, and this has led to the discovery of aluminium ethylate, $Al_2(C_2H_5O)_6$, alcohol in which the replaceable hydrogen is substituted by aluminium. It is a solid body at the ordinary temperature, but easily melts, and is capable of being sublimed unchanged, its vapour burning with a luminous flame and white smoke of the oxide of the metal. Other compounds prepared by this singular reaction, and the nature of the chemical changes which occur, are at present the subject of study.‡

[J. H. G.]

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* Further particulars respecting the decomposition of water by this special kind of electrolysis may be found in 'Proc. Royal Soc.' 1872, p. 218; 'Report Brit. Assoc.' 1872, Abstracts, p. 75; 'Journal Chem. Soc.' 1873, p. 452; 'Phil. Mag.' 1875, pp. 284, 285. The account of "Researches on the Action of the Copper Zinc Couple on Organic Bodies" is given in the 'Journal Chem. Soc.' 1873, pp. 445, 678, 961; 1874, pp. 208, 406, 410, 615; 1875, p. 508. See also vol. vii. of these 'Proceedings,' p. 521.

† 'Journ. Chem. Soc.' 1873, p. 541.

‡ Since this discourse was delivered, this peculiar reaction has been elucidated in a paper read before the Chemical Society, on "The Simultaneous Action of Iodine and Aluminium on Ether and Compound Ethers." An intermediate body, the aluminium iodoethylate, $Al_2(C_2H_5O)_3I_3$, is there described.

PHENOMENA ACCOMPANYING THE ELECTROLYSIS OF WATER WITH OXIDISABLE ELECTRODES.

By Professor GLADSTONE, F.R.S., and ALFRED TRIBE, F.C.S.

IN a paper read at the meeting of the British Association in 1872, we pointed out that " the electrolysis of water is more easily effected between poles made of a metal that has a considerable affinity for oxygen than between poles that have little affinity." It was also stated that " when zinc poles were used, there was found to be more than double the action that there was when platinum poles of the same size and at the same distance were employed," and that the order of efficiency seemed to be platinum, tin, silver, copper, iron, lead, zinc, magnesium.

In performing these experiments, we found a wearing away of the positive electrode, a formation of singular clouds and films in the liquid, and a growth of threads, fringes, or arborescent crystals of metal on the negative electrode. In the case of silver, when a thread of the metal touches the glass, it sometimes spreads over the surface as a thin translucent film, in which, however, a crystalline structure is easily discernible, but which is so thin that it appears green or purple by transmitted light.

Some of these phenomena were observed by D a v y, and even in the original electrolysis of water by Nicholson and Carlisle, who employed, in the first instance, brass wires for the passage of the electricity; but no explanation is given by these early observers.

The explanation, however, is not far to seek.

In the case of the more active metals, the oxygen, of course, is not given off at the positive electrode as gas, but it combines with the metal to form an oxide, or rather hydrate, and as all the hydrates are probably more or less soluble in water, there is soon formed a dilute solution of the metallic compound in the space between the electrodes. This probably offers less resistance to the voltaic current than the water itself, and is successively decomposed, the final result being the deposit of metal on the negative electrode.

This corrosion of the positive electrode is, perhaps, assisted by another circumstance. We know, from the experiments of Davy, that when carefully distilled water which has been exposed to the air, is decomposed by a powerful battery, a small quantity of nitric acid is formed at the positive pole from the dissolved nitrogen. This, of course, might be expected to facilitate the solution of the metal. We did not employ powerful batteries, but single cells of Daniell or Grove, and we sought for this nitric acid by the extremely delicate carbolic acid test, and for nitrous acid by the iodide of potassium and starch test. Sometimes a trace was detected, at other times none. That the presence of a nitrate is not essential to the production of the phenomenon was proved, in the case of silver, by taking a solution of pure hydrate of silver in the purest distilled water, and electrolysing it between platinum electrodes, when the usual beautiful arborescent crystals of metal were obtained.

A series of comparative experiments were made with electrodes consisting of narrow plates of zinc, lead, iron, copper, silver, and platinum, and with the purest water collected direct from the pipe of the still. One cell of Grove was employed for each pair of electrodes; the arrangements were made strictly comparable, the only difference consisting in the nature of the metal, and the results were observed at the termination of 3 minutes, 15 minutes, 1 hour, 4 hours, and 22 hours.

In the case of zinc, the positive electrode was slightly oxidised in 3 minutes, and afterwards was distinctly eaten away at the lower part. Bubbles of gas formed almost immediately, escaping from the inner side of the negative electrode; accompanied in 15 minutes with a slight cloudiness of the neighbouring liquid; and in an hour with the formation of a white substance adhering to the inner side of the plate, and a little black deposit fringing the lower part. This formation of oxide and metallic zinc increased, and at the end of 22 hours 1·5 c.c. of gas had been collected. The black deposit examined by the microscope was found to be crystallised zinc, and no trace of a nitrogen-compound could be detected in the solution.

In the case of lead, the positive electrode showed signs of slight oxidation, and the negative electrode a few small bubbles, in 15 minutes;

a slight cloudiness was then beginning to form, which afterwards increased; some oxide was found adhering in an hour; and afterwards grey metallic lead, which at the end of 22 hours was found to have stretched across to the positive electrode, forming a metallic connexion which was so much heated by the passage of the voltaic current that the liquid became warm. About 0·5 c.c. of gas was collected.

In the case of iron, the oxidation of the positive electrode was observed in 15 minutes, and at the end of the experiment it was almost black. On the negative electrode, a minute bubble or two and a faint cloud were observed in 3 minutes' time. A yellowish-red oxide soon made its appearance, and afterwards a whitish-green oxide, which turned red on exposure to the air. There was also a dark deposit of iron from which gas was evolved for some minutes after disconnecting the battery. This was doubtless due to the fact that finely divided iron decomposes water of itself. About 2·5 c.c. of gas were collected in the 22 hours.

In the case of copper, no tarnishing of the positive electrode was observed till the 4-hour period; but in 15 minutes, though there was no gas, there was a slight cloudiness in the liquid near the inner side of the negative electrode; in 1 hour, fragments of green hydrate adhered to it, and there was a growth of black from the lower edges. In 4 hours it was covered with black powder, while the growth at the edges increased. In 22 hours the gas produced was scarcely to be measured, but the black and red crystallised copper was considerable in quantity.

In the case of silver, a slight tarnishing of the positive electrode appeared in one hour, no gas formed at the negative electrode, but there was a cloudiness in 15 minutes, and a fringe of metal in one hour, which gradually extended till it joined the positive electrode, while the liquid, in consequence, became warm. The silver spread over the glass with its usual beautiful appearance.

In the case of platinum there was no visible result at all.

At the conclusion of the experiment, the water in which the iron electrodes had been immersed gave a faint blue tinge with ferrocyanide of potassium; the water, with the lead and copper electrodes, gave a faint, and that with the silver electrodes, a very distinct blackening with hydrosulphuric acid.

The comparative solubility of these metallic hydrates in water has, no doubt, great effect upon the ultimate result, though the different electromotive force, or affinity for oxygen, of the various metals must be looked upon as causing the initial difference.
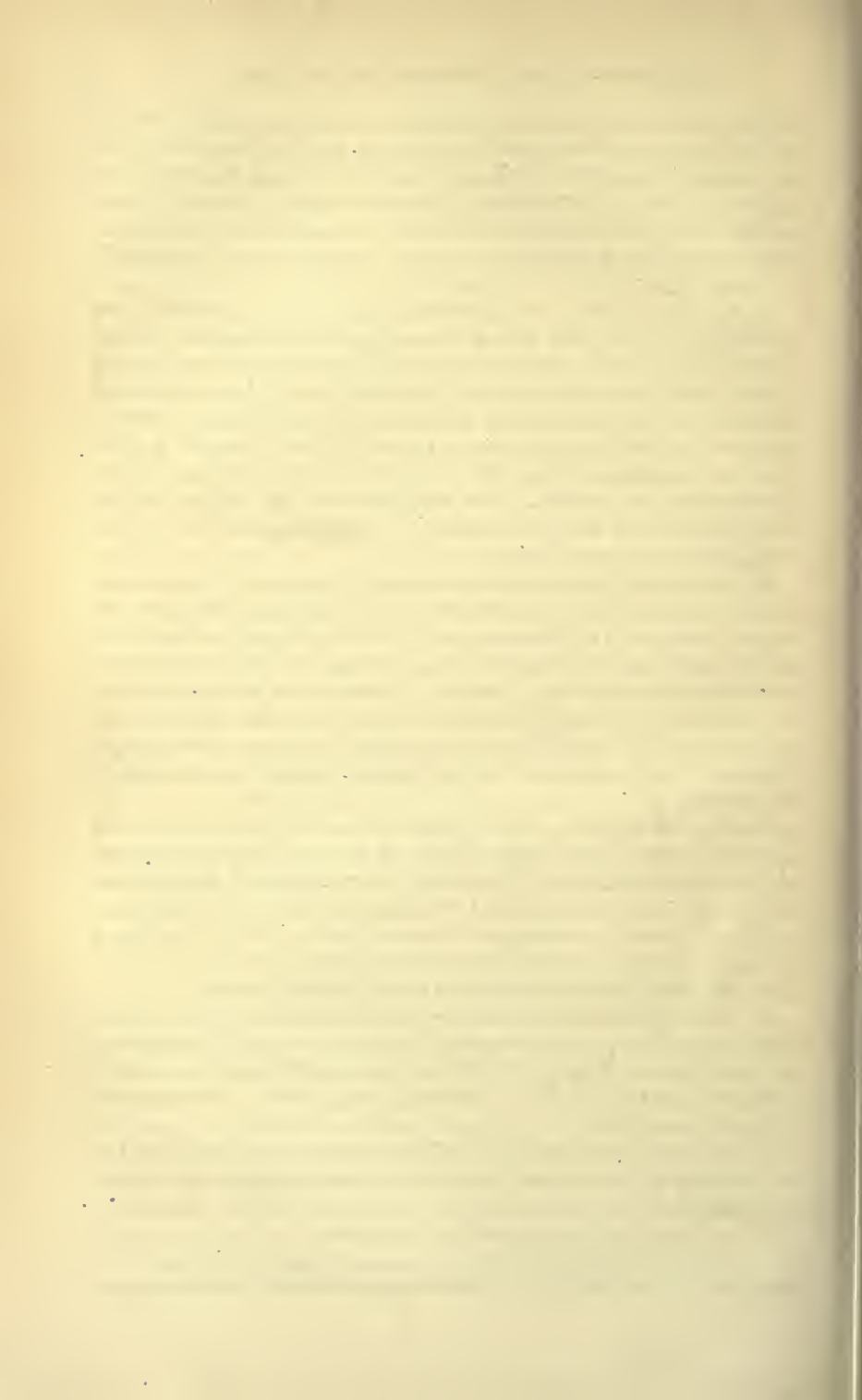
THE SIMULTANEOUS ACTION OF IODINE AND ALUMINIUM UPON ETHER AND COMPOUND ETHERS.

By J. H. Gladstone, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and Alfred Tribe, Lecturer on Chemistry in Dulwich College.

It is well known that aluminium has no action upon either water or alcohol; but in previous communications to this Society we have shown that in presence of aluminic bromide or iodide, an action immediately takes place, with production of alumina and hydrogen in the case of water, and of aluminic ethylate and hydrogen in the case of alcohol. This led us to expect that if ether were exposed to the action of the same agents, it might give us either ethyl and aluminic oxide, or ethyl and aluminic ethylate; and perhaps throw some light on the nature of the chemical change.

Upon trying the experiment, we found that ether remained unaffected, even when boiled with aluminium and aluminic iodide, but that an oily body formed when it was exposed to the simultaneous action of iodine and aluminium.

This reaction was investigated, and the following experiment illustrates the general course pursued and the results obtained :—

27 grams of iodine with 2 grams of finely cut aluminium foil, that is, rather more than an equivalent quantity of aluminium, were mixed in a flask, and 20 c.c. of pure ether were added. A sensible rise of temperature took place at once, and in a minute or so the ether boiled

violently, and was prevented from escaping only by an inverted condenser to which the flask was attached. This continued for about five minutes, when the action gradually ceased. The flask was now connected with an ordinary condenser and heated by immersion in boiling water, when a slightly brown ethereal liquid distilled, from which, by agitation with water, 3·5 c.c. of a body containing iodine and heavier than water separated. A brown semi-solid residue was left in the flask, and this was now slowly heated to 150° C. by immersion in a paraffin-bath, when again an oily body containing iodine distilled, which, after shaking with water, measured 6·5 c.c. ` On heating to a still higher temperature (200°), the residue frothed somewhat, and ·5 c.c. more of the oily body was obtained, making a total of 10·5 c.c.

The different portions of the oily body were added together, washed, dried, and subsequently distilled. It began to boil at 55°, and quickly rose to 70°, between which and 72° the greater part passed over. This portion resembled ethyl iodide in odour, had the same boiling point, and a specific gravity of 1·884 at 17° C., which agrees fairly with the known specific gravity of that body. When 5 c.c. (9·4 grams) were added to a copper-zinc couple wet with water, 1191 c.c. of gas burning with a luminous flame were obtained at the ordinary temperature in 28 hours. Assuming the body to be pure ethyl iodide, it should have yielded, under the circumstances, and according to our previous work, 1249 c.c. of ethyl hydride.

The residue left in the flask, after heating for some time at 200°, was light brown in colour, and weighed 14·59 grams. It dissolved almost completely in alcohol and water. On heating the entire residue from another experiment, over·a lamp, 200 c.c. of gas were obtained, of which 68·2 were absorbable by bromine, the remainder burning with a slightly luminous flame, and a residue was left in the flask which consisted of alumina with some iodine.

The formation of the ethyl iodide might be accounted for on the supposition—1. That the products are ethyl iodide and aluminic oxide. 2. That the products are ethyl iodide and aluminic oxyiodide or its elements. 3. That they are ethyl iodide and aluminic iodoethylate, or its elements. If the first of these were true, the residue, after distilling off the ethyl iodide would consist of alumina and be insoluble in water and alcohol, but as it is soluble in these menstrua, this supposition is negatived. If the second were true, the residue, consisting of oxyiodide, could certainly not have yielded hydrocarbons by heat. The inference is therefore, that the third supposition is in the main correct, but, as a somewhat greater quantity of ethyl iodide is pro duced than even this requires, the probability is that the iodoethylate slowly splits up into alumina and ethyl iodide under the influence of heat—a conclusion confirmed by the amounts of iodine and alumina

in the 14·59 grams of residue mentioned above. The quantities of these substances found were—

<div style="text-align:center">

Iodine . . . . 8·769

Alumina . . . . 3·866

</div>

If the iodine be calculated as aluminic iodoethylate, 13·135 grams of the residue are accounted for, which would be equivalent to 2·365 grams of alumina, leaving, therefore, 1·501 which, added to 13·135 equals 14·636. The close agreement of this number with the weight of the residue confirms the belief that it consists of aluminic iodo-ethylate with alumina, and leaves but little doubt as to the truth of the third supposition.

Aluminic Iodo-ethylate.

As we know nothing more about the properties of this body than what has been gathered from the study of the fixed product of the aluminium iodine and ether reaction, we sought for a process by which it could be prepared in a state of purity. As we had already suspected its presence in the reaction with alcohol (previously described by us), and as the proportions expressed in the equation—

$$6(C_2H_5O.H) + Al_2I_6 + Al_2 = 2Al_2\left\{ \begin{matrix} (C_2H_5O)_3 \\ I_3 \end{matrix} \right. + H_6,$$
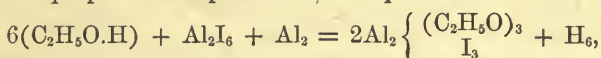
appeared likely to give the iodo-ethylate, the following experiment was made :—

29 c.c. of alcohol containing 8·294 grams of aluminic iodide in solution were added to 0·556 gram of finely-cut aluminium foil, the inorganic constituents being in the proportions required by the above equation. The flask containing the materials was heated by immersion in boiling water, when hydrogen was at once evolved, and this continued for 15 minutes, 688 c.c. of gas being collected, that is, 7 c.c. above the calculated amount.

The product of the action left in the flask, which can consist of none other than aluminic iodo-ethylate or its elements mixed with or in combination with alcohol, was a liquid of a brown colour and perfectly miscible with water, and on evaporation *in vacuo* it dried up to a non-crystalline semi-solid mass.

The whole of the non-gaseous product of an experiment similar to the above was heated in a distilling apparatus by immersion in boiling water. It gave off alcohol and a little ethyl iodide, leaving a non-crystallised brown mass. When this was heated between 100° and 200°, a little more alcohol passed over accompanied by a greater quantity (3 c.c.) of ethyl iodide, leaving alumina with a small quantity of iodine in the flask, which clearly indicates that the iodo-compound splits up, in presence of alcohol, into alumina and ethyl iodide at a high temperature.

The fact of this splitting up of the iodo-ethylate on distilling and heating with alcohol led us to expect that the residue from the iodine ether reaction, after heating to 200°, would also yield ethyl iodide on heating with alcohol. Such was found to be the case. It at the same time led us to expect that the whole of the iodine employed could, by the assistance of alcohol, be converted into ethyl iodide, which is practically shown to obtain by the following experiment:—

The product from 27 grams iodine, 2 grams aluminium, and 20 c.c. ether gave, on distilling at 100° C., 3·75 c.c. of ethyl iodide. 20 c.c. of absolute alcohol were now added, which occasioned a considerable evolution of heat, sufficient to drive over 1·75 c.c. of ethyl iodide. On heating first to 100° and then to 200°, in addition to alcohol, 9·5 c.c. of ethyl iodide passed over, making a total of 15 c.c., the theoretical quantity being 17·3 c.c. The residue left in the flask was almost white alumina, containing 1·4 gram of iodine.

Taking the whole of the facts above detailed into consideration, the simultaneous action of iodine and aluminium upon ether may be thus represented:—

$$3 \left\{ \begin{array}{l} C_2H_5O \\ C_2H_5 \end{array} \right. + Al_2 + I_6 = Al_2 \left\{ \begin{array}{l} (C_2H_5O)_3 \\ I_3 \end{array} \right. + 3C_2H_5I.$$
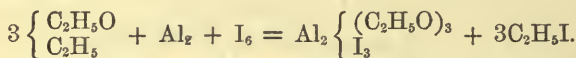
This action of heat upon the aluminic iodo-ethylate when associated with alcohol, may be represented thus:—

$$Al_2 \left\{ \begin{array}{l} (C_2H_5O)_3 \\ I_3 \end{array} \right. = Al_2O_3 + 3C_2H_5I,$$
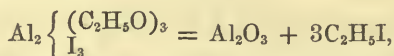
but it is probably the product of two actions, thus:—

(1) $Al_2 \left\{ \begin{array}{l} 3C_2H_5O \\ I_3 \end{array} \right. + 3 \left\{ \begin{array}{l} C_2H_5O \\ H \end{array} \right. = 3C_2H_5I + Al_2 \left\{ \begin{array}{l} 3C_2H_5O \\ (HO)_3 \end{array} \right.$

(2) $Al_2 \left\{ \begin{array}{l} (C_2H_5O)_3 \\ (HO)_3 \end{array} \right. = Al_2O_3 + 3 \left\{ \begin{array}{l} C_2H_5O \\ H \end{array} \right..$
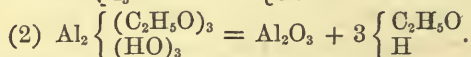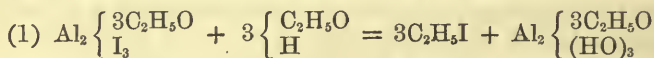
It might be anticipated that iodine and aluminium, if allowed to act simultaneously upon other ethers than the ethylic, would yield their corresponding iodides. Such the following experiment shows to be the case with amylic ether.

20 c.c. of this compound were added to a flask containing 2 grams of finely-cut aluminium foil, and 27 grams of iodine. There was no action apparent in 30 minutes, but soon afterwards the temperature was found to have risen sensibly, this quickly increased, and the action finished in 15 minutes.

The brown liquid left in the flask was heated by immersion in a paraffin-bath, slowly from the melting point of that substance, to 200° C. The distillate obtained after washing with water gave 15 c.c. of an oily body containing iodine.

It also appeared of interest to ascertain whether the reaction

described is a general one with bodies containing C_nH_{2n+1} radicals, or is applicable only to simple ethers. Experiments were accordingly made with the acetates of ethyl and amyl.

In one experiment with amyl acetate, 16·5 c.c. of this body were placed together with 13·9 grams of iodine and 1 gram of aluminium. The contents of the flask quickly rose in temperature, and the action became very energetic; it was over in 30 minutes. The flask was now slowly heated by a paraffin-bath to 200°, when an oily body containing iodine distilled, commencing at about 140°, and after agitation with water it measured 12 c.c. On drying with calcium chloride the greater part passed over between 137°—142°, and it had a sp. gr. of 1·44 at 11° C. As the boiling point of amyl iodide is said to be 146° and its sp. gr. 1·511, this product probably contained a little undecomposed acetate.

In an experiment with the ethyl compound, 9·3 c.c. of it were mixed with the same quantities of iodine and aluminium as in the previous experiment. The action was extremely violent, being nearly over in five minutes, and necessitating constant agitation of the flask in cold water. The flask was afterwards heated to 100° for thirty minutes to destroy the last traces of aluminium, and the temperature was then slowly raised to 200° C. An oily iodide distilled which, after washing with water, measured 7 c.c. On drying with calcium chloride and distilling, the whole boiled between 70°—72°, had a sp. gr. 1·98 at 9° C., and possessed the odour of ethyl iodide, with which it accords perfectly in boiling point and specific gravity. The theoretical quantity of ethyl iodide obtainable is 7·2 c.c.

The residues of both experiments consisted of aluminic acetate with a little iodide.

It is therefore evident that the metal in these reactions combines with the $C_2H_3O_2$ of the acetate, just as it does with the $C_nH_{2n+1}.O$ of the ethers, while the C_nH_{2n+1} immediately enters into union with iodine forming the iodide, thus :—

$$6\left\{ \begin{array}{l} C_nH_{2n+1} \\ C_2H_3O_2 \end{array} \right. + Al_2 + I_6 = 6\left\{ \begin{array}{l} C_nH_{2n+1} \\ I \end{array} \right. + Al_2(C_2H_3O_2)_6.$$
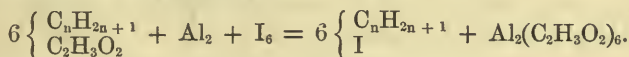
This last research has placed us in a position to form a more definite opinion as to the manner in which the peculiar chemical change recently described by us, is brought about. Water, alcohols, and ethers are well known to be analogous bodies, and each may be considered as binary compounds in which the radical H or C_nH_{2n+1}. is united to the oxygen compounds of a similar radical, thus :—

$$\begin{array}{lll} \text{Water} & \ldots\ldots & H.HO \\ \text{Alcohols} & \ldots\ldots & H.C_nH_{2n+1}.O \\ \text{Ethers} & \ldots\ldots & C_nH_{2n+1}.C_nH_{2n+1}O. \end{array}$$

Now aluminium shows a great tendency to combine with hydroxyl. We know, for instance, that an aqueous solution of acetate of aluminium will form the hydrate $Al_2(HO)_6$, and give acetic acid by boiling or diffusion; and the iodide, bromide, or chloride of aluminium exposed to damp air gives off free acid. Similarly, we believe, the aluminium is ready to combine with $C_nH_{2n+1}O$, if a halogen be present to remove the H or C_nH_{2n+1}.

Our present belief is that the chemical change takes place through the intervention of intermediate bodies, thus :—

$$(a.)\ Al_2I_6 + 3H_2O = Al_2{(HO)_3 \atop I_3} + 3HI.$$

$$(b.)\ Al_2{HO_3 \atop I_3} + 3H_2O = Al_2(HO)_6 + 3HI.$$

$$(c.)\ 6HI + Al_2 = Al_2I_6 + 3H_2.$$
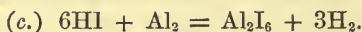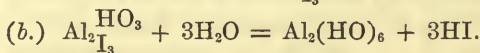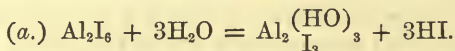
It will be understood that the complete hydration of the aluminium iodide, as by equation b, occurs only when the excess of hydriodic acid is destroyed, as by equation c, and thus the evolution of hydrogen will be continuous as long as aluminium and water are present, which accords with our experiments.

We find, moreover, that an aluminic iodo-hydrate corresponding with $Al_2{(HO)_3 \atop I_3}$ in composition readily dissolves in water, and when heated with aluminium gives an equivalent amount of hydrogen. We find also that an alcoholic solution of its carbo-hydrogen analogue also yields equivalent quantities of hydrogen when heated with aluminium. This tends to confirm the explanation above given, and also elucidates the decomposition of alcohol by the joint action of aluminium and its iodide, which may be represented in a similar way to the above, substituting the radical C_2H_5O for HO.

The reaction with ether is analogous to what occurs with water or alcohol according to equation (a), the elements being free, thus :—

$$Al_2 + I_6 + 3(C_2H_5.C_2H_5O) = Al_2 \left\{ {(C_2H_5O)_3 \atop I_3} + 3C_2H_5I. \right.$$
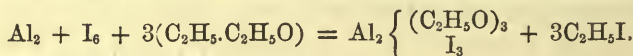
PREPARATION OF COPPER-ZINC COUPLES.

By J. H. GLADSTONE, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and ALFRED TRIBE, F.C.S., Lecturer on Chemistry in Dulwich College.

IN 1872 we communicated to the Royal Society the fact that zinc on which copper or some other negative metal was deposited in a spongy condition decomposes water at the ordinary temperature. This association of metals we subsequently termed the *copper-zinc couple,* an agent which has since been instrumental in the discovery of many new compounds and reactions.

Observations on the preparation of the couple have been published by Professor Thorpe and by ourselves, but the contemplation of a still larger extension of its use induced us to study more in detail the effect of the quantity and condition of the negative metal, with the practical object of arriving at the best formula for its preparation.

From the beginning we have used zinc in the form of foil. This condition possesses advantages. It gives a greater surface for equal weights than granulated zinc does, and admits of the use of a definite amount of surface, which is absolutely necessary where comparative results are required. The foil has generally been obtained from Messrs. Hopkin and Williams, 16, Cross Street, E.C. It contains about 1 per cent. of lead, the average amount of that metal which we found in several specimens of commercial zinc, and its thickness should be such that a square decimeter weighs about 2 grams.

Preparation of the Couple.

Well crumple the required quantity of foil, and cut it into pieces of from 100 to 600 square millimeters. Place these in a vessel suitable for the projected operation, add a solution of copper sulphate, and allow the whole to remain until decolorised. Pour away the liquid, which has become a solution of zinc sulphate, and thoroughly wash the couple so made with water. Should more copper be required than is obtainable from the volume of copper sulphate solution necessary for the complete immersion of the zinc, another "deposition" can be effected by replacing the solution of zinc sulphate produced in the first operation by more copper sulphate.

Influence of Quantity and Condition of the Copper.

When zinc displaces copper from equal volumes of its sulphate of different strengths, the quantity of the metal deposited varies of course with the strength of the copper solution. Its condition also varies very considerably. Separated from weak solutions it is perfectly black and adheres firmly to the zinc, and when the solution is very weak the coating is almost impervious, the latter circumstance tending rather to the protection of the zinc than to the increase of its activity. Separated from very strong solutions, the copper is chocolate coloured or red, less adherent, and more spongy, and the crystals of the negative metal larger, which might with good reason be thought also to have an adverse influence upon the activity of the couple.

From considerations so complex as these, it became evident that the only way of arriving at a knowledge of the most effective association of the metals was by making a series of comparative trials. The experiments, the results of which are tabulated below, were therefore instituted. In each 5 meters of foil, 5 centimeters wide, weighing about 60 grams, were crumpled and cut into pieces of about 600 square millimeters. The couples were made by allowing the foil to decolorise equal volumes (450 c.c.) of copper sulphate of varying strengths, and their activity was ascertained by measuring the hydrogen evolved when placed in contact with distilled water. The action was allowed to go on for four hours before collecting the hydrogen, to allow of the hydrogenisation of the dissolved oxygen. The first reading was taken in 16 hours, the second in 40 hours.

Percentage of copper sulphate.	Copper deposited in grams.	Average Temperature.	Hydrogen evolved reduced to 0° C. and 760 mm.		Average work done by each gram of copper.		
			16 hours.	40 hours.	Between 4 and 20 hours.	Between 20 and 44 hours.	Between 4 and 44 hours.
0·55	1	17·6° C,	33·5	113·3	33·5	79·8	113·3
1·1	2	,,	92·1	255·7	46·0	81·8	127·8
1·65	3	,,	156·9	415·1	52·3	86·0	138·3
2·2	4	,,	169·1	439·3	42·3	67·5	109·8
2·75	5	,,	223·6	494·7	44·7	54·2	98·9
3·3	6	,,	224·6	546·3	37·4	53·6	91·0
3·85	7	,,	252·8	599·8	36·1	49·5	85·7
4·4	8	,,	288·5	682·3	36·0	49·2	85·3
4·95	9	,,	305·4	731·2	33·9	47·3	81·2
6·0	11	18·6° C.	352·4	889·7	32·0	48·8	80·8
7·1	13	,,	389·8	988·0	29·9	46·0	76·0
8·2	15	,,	468·7	1147·3	31·2	45·2	76·4
9·9	18	,,	479·8	1183·7	26·6	39·0	65·7
11·5	21	,,	494·8	1217·5	23·5	34·4	57·9
13·2	24	,,	457·3	1161·2	19·0	29·3	48·3

These results are shown graphically on the following page :—

A represents the 4th column of the table.
B   ,,   5th   ,,   ,,
C   ,,   6th   ,,   ,,
D   ,,   8th   ,,   ,,

The horizontal figures show the copper, the vertical figures being the hydrogen.

The main result of these experiments is that the action is directly proportional to the time and the amount of copper deposited; but this is modified by at least three different circumstances :—

1. The gradual oxidation of the zinc, which must necessarily diminish the action proportionally in the higher members of the series, or in the longer time.

2. Something—probably the close texture of the coating—in the lower terms, which does not admit the full action to take place until we have a solution of about 1·6 per cent.

3. Something—probably the size of the base of the copper crystals—which materially interferes after about 11 per cent.

Thus, so far as this series of experiments shows, a solution of 1·6 per cent. is the most active per amount of copper deposited, and one of about 11 per cent. does the most active work.

In order to ascertain more accurately the action due to the condition and magnitude of the copper crystals, we repeated our experiments,

depositing the same amounts of copper in a series of trials, but from different strengths of copper sulphate. The particulars are given in
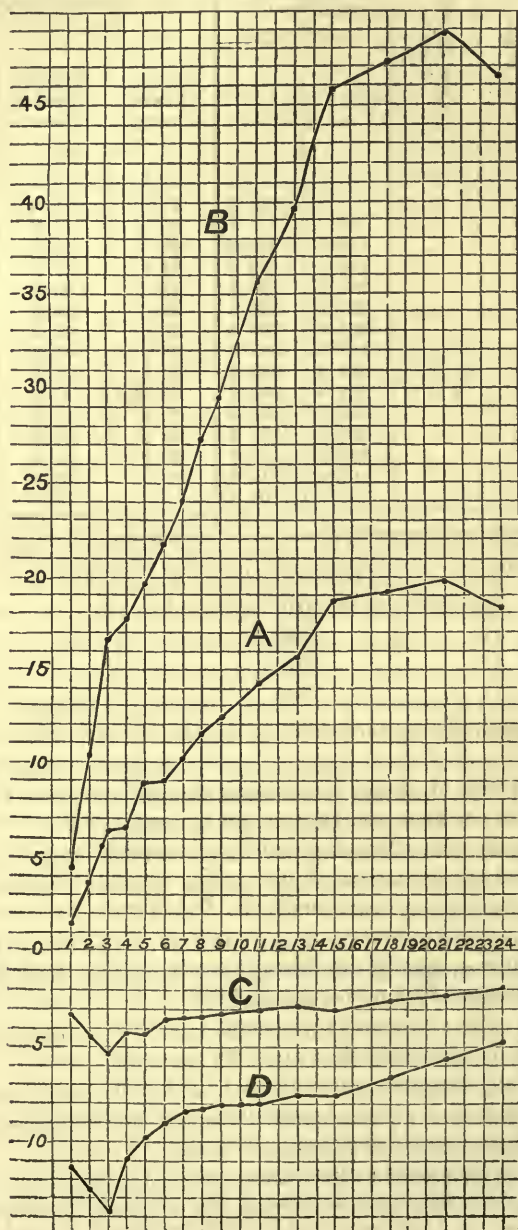
the subjoined table. The "number of depositions" means that one, two, &c., equal volumes of copper sulphate solution were successively decolorised.

Strength of copper sulphate.	Number of depositions.	Amount of copper in grams.	Average temperature.	Hydrogen evolved reduced to 0° C. and 760 mm.	
				16 hours.	40 hours.
11·0	1	20	17·4° C.	338·4	762·3
5·5	2	,,	,,	441·8	988·1
3·7	3	,,	,,	522·0	1124·9
5·5	1	10	,,	193·9	476·5
2·7	2	,,	,,	244·3	573·8
1·8	3	,,	,,	375·9	818·6
11·0	1	20	18·5° C.	430·8	972·7
2·8	4	,,	,,	561·9	1335·4
1·8	6	,,	,,	613·4	1463·2
1·4	·8	,,	,,	515·6	1273·4
5·5	1	10	,,	300·0	730·4
1·8	3	,,	,,	421·4	977·0
1·4	4	,,	,,	468·7	1118·9
0·7	8	,,	,,	450·0	1095·5

A glance at the results of each of the above series of experiments confirms the conclusion previously arrived at—that the most active couple is made when the solution contains about 1·4 to 1·8 per cent. of the salt.

The practical result is, therefore, that with the zinc employed the maximum effect is produced when the 20 grams of copper are deposited from about 1·4—1·8 per cent. solution of copper sulphate in from six to eight depositions.

Assuming 1·8 as the best strength of copper sulphate to employ, it became necessary to ascertain how much copper it was desirable to deposit upon a given surface of zinc. The following series of experiments was therefore made :—

Strength of copper sulphate.	Number of depositions.	Amount of copper in grams.	Average temperature.	Hydrogen evolved, reduced to 0° C. and 760 mm.	
				16 hours.	40 hours.
1 ·8 per cent.	1	3 ·19	16 ·4° C.	99 ·1	306 ·3
,,	2	6 ·38	,,	226 ·5	591 ·1
,,	3	9 ·57	,,	330 ·4	819 ·1
,,	4	12 ·76	,,	382 ·3	914 ·7
,,	5	15 ·95	,,	490 ·8	1131 ·5
,,	6	19 ·14	,,	566 ·4	1345 ·7
,,	7	22 ·33	,,	612 ·9	1297 ·3
,,	8	25 ·52	,,	594 ·1	1334 ·9
,,	9	28 ·71	,,	641 ·2	1443 ·4
,,	10	31 ·9	,,	565 ·8	1358 ·5

It is evident that the activity of the couple increases with the larger amount of copper till the sixth or seventh deposition, after which there is little or no advantage.

In consequence of these experiments, and in order to avoid multiplying depositions, we have adopted, as the most convenient method of obtaining a very active couple, a solution of 2 per cent. of copper sulphate, in sufficient quantity to yield 20 grams of copper on the zinc employed.

Ethyl Hydride.

In certain reactions it is of advantage, as in the preparation of the hydrides of the alcohol-radicles, that the couple should act upon mixtures of alcohol and haloïd ethers in absence of water. All that is to be done in such cases is to wash the water couple a few times with alcohol, and add the haloïd compound alone or in admixture with alcohol. But it was necessary to ascertain whether the formula which gives a couple of maximum activity for water, would also yield the most effective couple for this class of decompositions.

Six experiments were made on the decomposition of precisely the same amounts of ethyl iodide and alcohol. The couples used were made of the same zinc foil, one-fourth of a meter in length, and were washed with alcohol. The volume of copper sulphate decolorised at each deposition measured 21 c.c., and the temperature during the experiments varied from 15—16° C. The results are given in the annexed table.

Percentage of copper sulphate.	Number of depositions.	Copper in grams.	Ethyl hydride in c.c.		
			15 mins.	1 hour.	25 hours.
2	1	·166	7*	28	514
,,	2	·333	23	56	535
,,	3	·499	56	—	632
,,	4	·666	64	94	692
,,	5	·832	71	115	722
,,	6	·999	68	113	767

The augmentation of action for equal increments of copper is more rapid here than in the series of experiments with water. For practical purposes, however, it may be taken that a couple which decomposes the maximum amount of water in a given time would also yield the greatest amount of ethyl hydride by its action on a mixture of ethyl iodide and alcohol.

The time taken up in depositing a given weight of copper depends very much upon the number of depositions. With the view of ascertaining more specifically whether these could be lessened with practical advantage, we deposited the same weight of copper on equal quantities of the foil, firstly from a 6 per cent. solution in two depositions, secondly from a 2 per cent. solution in six depositions. The results were as under :—

6 per cent. solution in } Hydrogen in 16 hours,   745 c.c.
  two depositions .. }   ,,   40   ,,   1430 c.c.
2 per cent. solution in } Hydrogen in 16 hours,   878 c.c.
  six depositions .... }   ,,   40   ,,   1515 c.c.
6 per cent. solution in } Ethyl hydride in 1 hour, 94 c.c.
  two depositions.... }   ,,   ,, 25 hours, 620 c.c.
2 per cent. solution in } Ethyl hydride in 1 hour, 147 c.c.
  six depositions .... }   ,,   ,, 25 hours, 628 c.c.

It is evident that a 2 per cent. solution gives the better result.

Dry Couples.

In the preparation of certain of the organo-zinc compounds and other reactions, it is absolutely necessary to employ the couple in a dry condition. For this purpose wash the well-washed water couple with alcohol (strong methylated), then with ether. Pour off the ether, and dry the couple in a current of hydrogen-gas,† heating the

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* The solubility of ethyl hydride in the mixture doubtless affected this number.

† Hitherto we have used carbonic acid. We now recommend hydrogen or dry coal gas, because we have noticed that the couple when heated at all strongly in presence of carbonic acid, decomposes it, yielding carbonic oxide and oxide of zinc, the formation of the latter of which lessens the activity of the couple.

vessel containing it over a lamp. When the ether has escaped, heat
the couple a little more strongly, keeping it gently agitated. At a
certain point the couple breaks up, and becomes reduced to about a
tenth of its original bulk. It should be granular and not powdery.
Allow it to cool in hydrogen.

The time required to convert a given weight of ethyl iodide into
zinc ethiodide (which may be taken as a typical action) by means of
the dry couple, varies very much with the amount of the negative
metal. The results of some of our experiments on this point are
below. In each experiment half a meter of the foil was used, the
volume of copper sulphate for each deposition being 42 c.c. The
flasks containing the couples and 5 c.c. of ethyl iodide were attached
to an inverted condenser, and heated by immersion in boiling water.
As soon as the dropping ceased from the condenser, the conversion
was deemed complete.

Percentage of copper sulphate.	Number of depositions.	Copper deposited in grams.	Time for conversion into ethiodide in minutes.
1*	1	0·083	14 minutes.
1	2	0·333	12·5 and 14
2	1	0·333	6 and 9
2	2	0·666	9
2	4	1·333	26

Here it is seen that one deposition from a 2 per cent. solution of
copper sulphate gives a dry couple of maximum activity. The weight
of zinc used to the copper is in the ratio of $1 : 0\cdot036$. The reason why
so small a quantity of the negative metal produces the best result, is
not difficult to give. On drying, the projecting copper crystals doubt-
less, when of any length, undergo disintegration, thereby breaking
metallic contact with the zinc. The bases, however, of these crystals
adhere firmly, and this is probably the only portion of the deposited
copper which assists in the action.

The quantity of gaseous hydrocarbons produced in the first three of
the above experiments was nearly the same, measuring 4·7 c.c., which
means a loss of about 0·03 gram of ethyl iodide out of 9 grams. To
obtain a knowledge of the actual advantage of the couple, an experi-
ment was made as follows. Half a meter of the zinc foil was crum-
pled and cut into small pieces, washed with alcohol and ether, and
reduced while hot by agitation to about the same bulk as were the
couples. The time required to convert 5 c.c. (9·5 grams) of ethyl

* Only half the volume was used in this experiment.

iodide at about 100° C., was about 3 hours and 20 minutes, and the amount of hydrocarbons collected measured 164 c.c., which means a loss of 1·14 gram of the iodide. Thus zinc containing about 1 per cent. of the negative metal lead, takes 26·5 times as long in doing the same work as does the dry couple, and causes 34·5 times the loss by destroying the substance it is desirable to conserve.

Were pure zinc employed, the difference would doubtless be even more strongly marked, because after the surface of the zinc has been slightly corroded, any lead present as an impurity must act, to a greater or less extent, the part of the copper in our couple. This supposition was subsequently confirmed by the following experiment :—

Some zinc was reduced by ourselves, starting with pure sulphate, and without touching anything but porcelain. A quantity of this zinc was granulated, and the finer portions were picked out. 10·31 grams were heated for $6\frac{1}{2}$ hours with 5 c.c. of ethyl iodide. The flask was then washed out with anhydrous ether, water was added, the solution evaporated, and the zinc in solution determined. Zinc oxide found 0·0051 gram. The same zinc was then coupleised, and heated with the same amount of ethyl iodide. In 3 hours 25 minutes, the action was over, the flask was washed out with ether, the solution added to water, and precipitated by sodium carbonate. Zinc oxide found = 2·692 grams. These data give for equal times an amount of action 1004 times greater in the case of the couple than in the case of pure zinc.

In the conversion of ethyl iodide into the ethiodide on a larger scale, the temperature rises so quickly as frequently to necessitate the application of cold water to the flask. We have noticed that the mere heating of the ethiodide to 100° C. slowly evolves hydrocarbons. To prevent loss therefore, the conversion should be got over as quickly as possible. We have noticed too, that sometimes a small quantity of free zinc-ethyl in addition to the ethiodide is formed in the reaction, especially when it is carried on on a large scale, which flowing down the inner tube of the condenser, may give the impression of the non-conversion of the whole of the iodide.

We do not recommend granulated zinc for larger operations, from the impracticability of ascertaining the surface of any given weight of it; but we see no reason why the ordinary thin sheet zinc of commerce should not be used, which would avoid the employment of the more expensive foil.

In an experiment employing 4 meters of foil coated with 6·72 grams of copper deposited from a 2 per cent. solution of copper sulphate, and 60 c.c. of ethyl iodide (115 grams), we obtained within two hours, which includes the preparation of the couple, the conversion

into ethiodide, and subsequent distillation, 40 grams of perfectly clear zinc-ethyl, or 88·4 per cent. of the theoretical quantity, which is 18·7 per cent. in excess of what we obtained in the best operation, on one-twelfth the scale, described in our original paper on this subject.

The following are the recommendations, relative to the best proportions of zinc, and the strength and quantity of the copper sulphate to be employed in the preparation of copper-zinc couples, based on our results.

Dry Couples.—Add 84 c.c. of a 2 per cent. solution of anhydrous copper sulphate to 1 meter of foil 5 centimeters wide, that is 500 square centimeters, exposing on the two sides a surface of 1000 square centimeters, crumpled as directed.

Couples wet with Alcohol or Water.—To 1 meter of the same foil, add 84 c.c. of a 2 per cent. solution of the sulphate, allow the solution to decolorise, pour off the zinc sulphate, and repeat five times.

We would now draw attention to a few points which appear of special interest in connection with the action of the couple.

It is known that zinc does not decompose liquid water at any temperature at the ordinary pressure, but that the couple does even at as low a temperature as 2° C. It is known also that water is electrolyzed by a small battery power. Again, zinc at the ordinary temperature has no action upon a mixture of ethyl iodide and alcohol, whereas the couple decomposes it readily. Yet no signs of electrolysis could be detected when this mixture was submitted to the action of 100 Grove's cells, even when the platinum electrodes employed were very close together.

It would appear then that this simple association of metals is more powerful for effecting the decomposition of certain organic bodies, than the electric power derivable from a large battery.

Note on the Electrolytic Conduction of some Organic Bodies. By J. H. Gladstone, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and Alfred Tribe, F.C.S., Lecturer on Chemistry in Dulwich College.

During our early researches[*] on the copper-zinc couple it naturally occurred to us that we were employing a special means of electrolysis acting at insensible distances; but the first organic substances which we succeeded in decomposing by means of this agent were such as are usually considered non-electrolytic—for instance, iodide of ethyl; and we obtained the remarkable result that when some of these were mixed with alcohol they were much more readily decomposed, although pure alcohol itself is not attacked by the couple of dissimilar metals. From time to time we experimented with external batteries of 10 or 50 cells of Grove, in order to obtain some direct evidence of the electrolyzability of these compounds in the ordinary way, but with only negative results. On the 26th of April, 1875, however, we made a series of experiments, employing 100 Grove's cells, and obtained results which we did not pursue further at the time, but which we think interesting, especially in connexion with the experiments on other but similar bodies which Dr. Bleekrode has lately communicated to the Royal Society, and a short notice of which appears in the last Number of its ' Proceedings.'

We used for the experiments a glass tube, about 5 millims. diameter, closed at one end, into which were fused two platinum wires, about 1 millim. apart. The liquids were placed in this tube, and the wires connected with the terminal wires of the battery, an ordinary astatic galvanometer being placed in the circuit. The results obtained are as follows:—

Ethyl Iodide.—Nil.

Alcohol.—On making contact the galvanometer-needle showed a deflection of 20°, and a slight commotion of the liquid was observable. The alcohol gradually warmed up until it boiled, the deflection of the needle increasing the whole time. Gas was apparently given off in minute quantity from the negative electrode; but it was difficult to be certain of this.

Equal volumes of Alcohol and Ethyl Iodide.—There was a deflection of 30° on making contact, gradually rising. Great commotion ensued, the liquid rapidly circulating round the poles, as in the annexed diagram,

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[*] Proc. Roy. Soc. 1872, p. 218. Journ. Chem. Soc. 1873, pp. 445, 678, 961; 1874, pp. 208, 406, 410, 615; 1875, p. 508.

accompanied by a browning of the liquid. Not certain about the evolution of gas—apparently a few minute bubbles from the positive pole. The liquid boiled in about 4 minutes, the deflection being then 60°.

Ethyl Bromide.—Nil.

Equal volumes of Alcohol and Ethyl Bromide.—Violent commotion on making contact, the galvanometer being deflected to the stops. The liquid quickly boiled. Gas apparently given off from the negative electrode.

Chloroform.—Nil.

Equal volumes of Alcohol and Chloroform.—Violent commotion. Deflection to stops. The mixture very quickly boiled.

Ethyl Acetate, Propylene Bromide, Amyl and Isobutyl Iodides gave negative results. When mixed with equal volumes of alcohol they behave similarly to the mixtures referred to above.

Our results, preliminary as we considered them to be, show that the iodides of ethyl, isobutyl, and amyl, the bromides of ethyl and propylene, the acetate of ethyl, and chloroform are practically non-conductors to a battery-power of 100 cells Grove, and that alcohol is to some extent traversed by the current. They show also that when these liquid non-conductors are mixed with the feeble conductor alcohol, the conductivity of the mixture is greater than that of alcohol alone, which offers at least a partial clue to the readiness with which such mixtures are decomposed by the copper-zinc couple.

The very considerable development of heat in these liquids, which conduct the electric current with great difficulty, is a circumstance worthy of notice. In these cases it is evident that it does not result from any chemical change, because the decomposition, if any thing at all, is utterly insignificant in amount.

ON

SOME POINTS CONNECTED

WITH

THE CHEMICAL CONSTITUENTS OF THE SOLAR SYSTEM.

BY

J. H. GLADSTONE, Ph.D., F.R.S.,
PRES. C.S.*

IN a recent course of lectures on the Chemistry of the Heavenly Bodies, various considerations occurred to me, which are not to be found in the ordinary treatises on the subject. I have since found that Mr. Norman Lockyer's recent lecture at Manchester deals with some of these; but the following are, as far as I am aware, novel, and may be worthy of record as a contribution to a line of thought which is being at present considerably developed.

I. The discoveries by means of the spectroscope, and the general advance of knowledge of the heavenly bodies, have tended greatly to confirm the nebular theory of the creation of worlds. Assuming a hot nebulous mass made up of many different chemical elements gradually condensing towards a centre, the question arises, How will these elements be distributed? This would depend upon two different circumstances

* Read at the British Association, August 1877.

of a physical nature.   (1) Of course the cooling of such a nebulous mass must take place from its outer portion, giving rise to a distribution of temperature greatest at the centre and gradually decreasing towards the circumference.   One of the results of this would be that the least volatile constituents near the circumference would condense and sink towards the centre of gravity, forming eventually the liquid or solid nucleus, while the most volatile would still extend to the outermost portions of the nebula ; and the rest would arrange themselves in the order of their volatility, condensing into cloud at various distances from the intensely heated centre.   (2) But there is another law regulating the arrangement of the gases, which has been pointed out and mathematically proved in a paper communicated to the Royal Society by Mr. G. Johnstone Stoney as far back as May 1867*.   He concludes it " to be a necessary consequence of the molecular constitution of gases that in such an atmosphere, decreasing in temperature from within outwards, the various constituent gases are not everywhere equally mixed, but that in the upper regions those that have the lightest molecules rise the furthest, so that the gases overlap one another in the order of the masses of their molecules." We may therefore expect to find the chemical constituents arranging themselves according to their molecular masses so long as they retain their gaseity, and also according to their volatility when condensation has ensued.   In either case, however, the separation between the constituents would be far from perfect.   The lower stratum of the gaseous envelope will, of course, consist of all the gases diffused together ; and while the lighter gases outreach the heavier ones, still the molecules of a heavier gas, shooting about in all directions, will often approach the outer limits of a lighter one.   Every one also who has performed a fractional distillation knows how difficult, or rather impossible, it is to separate entirely one body from another by means of the difference in their boiling-points. Now this exactly represents what we actually find in the sun itself.   Stretching far beyond its luminous sphere there is an enormous atmosphere of hydrogen, which is by far the lightest of all the gases, and at the same time the least condensable of those which have been recognized in the sun.   Far into this atmosphere of hydrogen rise small quantities of sodium and magnesium, both volatile metals, and both giving vapours of exceptional lightness.   Lower down we find in large quantities the vapour of iron, certainly a less volatile metal, and

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* Proceedings of the Royal Society of London, vol. xvi. p. 25, and vol. xvii. p. 1.

having a greater molecular weight. This is accompanied by other metallic vapours of a similar degree of lightness, which probably condense to form that region of cloud which constitutes the glowing surface that we behold. The spectroscope has shown the absence in the solar atmosphere of mercury, tellurium, bismuth, and antimony, bodies of high molecular weight, which have been detected in Aldebaran—and, indeed, of all the metals of high atomic weight, except perhaps barium and traces of lead. At the same time we find no indication of any of the very infusible metals, such as platinum or gold. As to the centre of the sun itself, we are of course perfectly ignorant of its chemical constitution.

II. Let us now suppose the whole solar system to have been a great revolving nebula condensing to the central sun, and forming from its outer portion such globes as the planets and their satellites, or such accumulations of smaller particles as the comets, meteorites, the group of asteroids, or the rings of Saturn. How may we expect to find these bodies constituted? Clearly we may expect to find that they consist principally of those elementary substances which give the lightest or the least condensable vapours, while at the same time we may expect them to contain smaller quantities of the less volatile and of the heavier ones. Now the earth, though it is one of the planets nearest the sun, must still be regarded as formed from the external part of the great nebula, when we bear in mind the immense mass of the central sun itself. It became of interest to see whether the relative quantities of the known chemical elements in the earth was in conformity with this hypothesis. I asked two of my assistants to draw out a list of the elements, dividing them according to their abundance or otherwise on the surface of the globe. I did not construct this Table myself, lest in any instances my judgment should be warped by the theory which it was intended to test. The following is the Table which they drew up:—

Elements and Vapour-densities.

Non-metallic Elements.

Plentiful.		Not plentiful.	
Oxygen	16	Phosphorus	62
Silicon	28·5	Fluorine	19
Carbon	12	Bromine	80
Hydrogen	1	Boron	11
Sulphur	32	Iodine	127
Chlorine	35·5	Selenium	79
Nitrogen	14	Average	63
Average	19·8		

Metals.

Plentiful.		Rare.		Very rare.	
Aluminium ..	27·5	Cadmium ..	56	Platinum....	197·4
Calcium	40	Cobalt	58·8	Palladium ..	106·5
Sodium	23	Bismuth	208	Iridium	198
Magnesium ..	24	Tungsten....	184	Osmium	199
Potassium ..	39	Gold	196·7	Rhodium....	104
Iron	56	Strontium ..	87·5	Ruthenium ..	104
Manganese ..	55	Uranium	120	Lithium	7
Average ..	37·8	Molybdenum	92	Thallium....	204
		Glucinum ..	14	Vanadium ..	137
Common.		Titanium	50	Cerium......	92
Barium	137	Average..	106·7	Lanthanum..	92
Zinc	32·5			Didymium ..	96
Lead........	207			Yttrium	68
Arsenic	150			Thorium	231·5
Copper......	63·5			Niobium	97·6
Antimony ..	122			Cæsium	133
Silver	108			Rubidium ..	85
Tin	118			Indium	74
Chromium ..	52·5			Tantalum ..	137·5
Mercury	100			Tellurium ..	128
Nickel	58·8			Zirconium ..	90
Average ..	104·5			Average..	122·9

Note.—The numbers represent the atomic weights. It is very possible that the vapour-densities of many of the metals may really be represented by these numbers divided by two, as we know it to be in the case of zinc and others. If this be so, it will not affect the general conclusions.

It will be seen that the average density of those non-metallic elements which are plentiful is 19·8, against 63·0 as the density of the rarer ones. This contrast is still more striking in regard to the metals :—those in the list headed "plentiful" having invariably low vapour-densities, with the average of 37·8 ; those denominated "common" being nearly always higher, with the average of 104·5 ; those denominated "rare" averaging 106·7 ; while the very rare metals have almost invariably high atomic weights, giving the higher average of 122·9. This classification, however, scarcely represents the whole truth, especially in regard to the metals ; for as far as we are acquainted with the constituents of the earth, the first six or seven metals are incomparably more abundant than the remainder, while most of the heaviest metals exist but in merest traces. It may also be remarked that not one of the very rare metals is sufficiently volatile for its vapour-density to have been taken. This is quite in accordance with theory, showing that all those elements of which the great mass of the earth is composed are of low density when in the gaseous condition, and that they are mixed with much smaller quantities of bodies which as a rule give heavier and more condensable vapours.

III. The meteoric stones which fall to the earth from interplanetary spaces show this preponderance of the lighter elements still more strikingly. We have the advantage in their case of knowing what is in the interior as well as on the surface, which we do not know of our own globe; but, on the other hand, we know little or nothing of the atmosphere which, by analogy with the other heavenly bodies, we may suppose to surround each meteoric mass before it mixes with our own air. The various known constituents may be classified as follows :—

Elements of the Meteorites.

Plentiful.	Common.	Rare.
Iron.	Carbon.	Vanadium.
Magnesium.	Phosphorus.	Titanium.
Calcium.	Copper.	Tin.
Silicon.	Sodium.	Potassium.
Oxygen.	Cobalt.	Lithium.
Sulphur.	Manganese.	Chlorine.
Nickel.	Hydrogen.	
Chromium.		
Aluminium.		

IV. While the above tables give a general result which is unmistakably in accordance with the deductions of theory, there are evident exceptions in detail. Thus bismuth, which has nearly the heaviest of all vapours, is by no means the rarest constituent of the earth; but then it must also be remembered that it is one of the most volatile metals, and thus would remain in the atmosphere. On the other hand, glucinum, with the atomic weight of only 14, is amongst the rare metals; and lithium, the lightest of all, being only 7, is very small in quantity upon the surface of the earth. Lead, again, with the atomic weight 207, is common. A very natural way of accounting for such exceptions is to suppose that in the original nebula there was but a comparatively small quantity of glucinum and lithium, and a very large quantity of lead; for of course there is no reason to suppose that the nebulous mass was composed of 60 or 70 elements in equal quantities. There is another circumstance which may be expected to interfere with the universality of this rule : compound bodies differ both in volatility and density from the elements from which they are formed, and often without any reference to the mean of their respective quantities. Thus, to take the most familiar instance—water. Oxygen and hydrogen are gases which we have never succeeded in liquefying by any degree of cold or pressure; but the vapour of their compound

AN INQUIRY INTO THE ACTION OF THE COPPER-ZINC COUPLE ON ALKALINE OXY-SALTS.

By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, F.C.S., Lecturer on Chemistry in Dulwich College.

Part I.

In 1873 Professor Thorpe established the fact that the copper-zinc couple in presence of nitre and water converts the whole of the nitrogen of the salt into ammonia. Some months prior to the publication of his paper it had been noticed by ourselves that the couple quickly reduces an aqueous solution of this salt into nitrite of potassium.

This reduction first to nitrite, then to ammonia, is of considerable interest, and appeared to us to call for a more extended study. A close observation of the course of the chemical change we thought might reveal Dr. Diver's hyponitrite about which so little is known, and perhaps lead to the real explanation of this and similar reactions, about which nothing definite has yet been ascertained.

The couples used in this research were made by adding 100 c.c. of a 2 per cent. solution of copper sulphate twice to every meter of zinc foil 5 centimeters wide.

Potassium Nitrate.

We give the details of two experiments on the reduction of this salt. The nitrite and ammonia were each estimated daily at about the same

hour; the ammonia by the Nessler method, the nitrite by potassium permanganate.

In the first experiment 4 meters of foil were used, and 500 c.c. of a 1·2 per cent. solution of the salt; in the 2nd, 8 meters of foil and 640 c.c. of a 2·47 per cent. solution. The results are given below :—

Expt. I.

Time.	Temperature. Centigrade.	Percentages in grams.		Equal to KNO_3 reduced.	Work done each day expressed in milligrams of Hydrogen.*
		KNO_2.	NH_3.		
1 day	15°—17°	0·673	0·012	0·871 gram	107·8
3 days	,,	0·820	0·025	1·123 ,,	23·3
4 ,, ...	,,	0·778	0·03	1·103 ,,	6·6
5 ,, ...	,,	0·704	0·0425	1·09 ,,	19·5
6 ,, ...	,,	0·589	0·072	1·127 ,,	51·3
7 ,, ...	,,	0·347	0·1212	1·132 ,,	78·6
7 days 12 hours ..	,,	0·150	0·184	1·24 ,,	215
8 ,, ...	,,	Nil	—	—	—

Expt. II.

Time.	Temperature. Centigrade.	Percentages in grams.		Equal to KNO_3 reduced.	Work done each day expressed in milligrams of Hydrogen.*
		KNO_2.	NH_3.		
4 hours	17	0·526	0·006	0·66 ,,	583·6
1 day	13	1·182	0·022	1·535 ,,	241·7
2 days	14	1·429	0·036	1·912 ,,	74·2
3 ,, ...	14·5	1·587	0·0456	2·157 ,,	47
4 ,, ...	14·5	1·587	0·07	2·302 ,,	62·5
5 ,, ...	15·5	0·758	0·256	2·422 ,,	342·4
5 days 6 hours ..	17	Nil	0·40	2·376 ,,	955·2

During the progress of the experiments, hyponitrite was tested for with silver nitrate twice daily, but in every case with a negative result. The amount of permanganate used up in the estimations during the latter part of the action, jointly with the ammonia formed, points not only to the non-formation of this hyponitrite, but also of any body requiring for its oxidation more permanganate than the nitrite.

The course of this chemical change is remarkable. It starts somewhat energetically, then diminishes considerably, again increases, and finally ends more rapidly than it began. Ammonia and its equivalent of potash increase but slowly from the commencement until the time when the maximum amount of nitrite is produced, when this salt rapidly gives way, accompanied of course by an increasing amount of

* Calculated in accordance with equations :—

$$(a.)\ KNO_3 + H_2 = H_2O + KNO_2,$$
$$(b.)\ KNO_3 + H_8 = KHO + 2H_2O + NH_3.$$
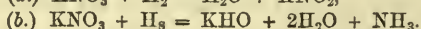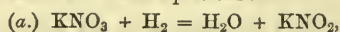
the alkalies. This rapid breaking down of the nitrite is coincident with the renewed activity of the couple, and it might therefore be thought that it is a consequence of the smaller stability of the nitrite; but this can scarcely be the explanation, since we see that almost from the very commencement the couple elects to deoxidise the nitrate, when it has the opportunity of attacking the nitrite.

The question therefore arises, are the variations in the amount of the action, especially the acceleration, due to the ammonia and potash produced? The following series of experiments show the influence of these bodies on the amount of hydrogen set free. The first column represents the hydrogen from a couple immersed in water alone; the second and third from similar couples immersed in similar volumes of aqueous solutions of NH_3 and KHO respectively. The strengths of the solutions of ammonia and potassium hydrate in each set of experiments approximate to the equivalent proportions. The gas measurements were taken after two hours.

In Expt. A, the strength of NH_3 used was 0·026 per cent.; KHO, 0·087 per cent.

In Expt. B, the strength of NH_3 used was ·0256 per cent.; KHO, 0·846 per cent.

In Expt. C, the strength of NH_3 used was 0·51 per cent.; KHO, 1·69 per cent.

In Expt. D, the strength of NH_3 used was 20·0 per cent.; KHO, 65·8 per cent.

Taking the action of the water couple in each set of experiments as unity, the numbers below express the relative quantities of hydrogen obtained:—

	Water.	Ammonia.	Potash.
A	1	1·8	2·0
B	1	1·75	2·75
C	1	0·91	2·27
D	1	0·36	1·59

from which it appears that the two weakest ammonia solutions augment the action, while the stronger undoubtedly diminish it. The influence of potash is always an accelerating one, but the effect is at the maximum when the alkali is present in comparatively small quantity. These unexpected results were corroborated by the following series of experiments with different strengths of the alkalies.

In I, ammonia, 0·21 per cent. was used; in II, 0·41 per cent.; and in III, 0·78 per cent.

In IV, potash, 0·65 per cent. was used; in V, 1·27 per cent.; and in VI, 2·12 per cent.

Time.	Temperature. Centigrade.	Hydrogen in c.c. reduced to 0° and 760 mm.					
		Ammonia.			Potash.		
		I.	II.	III.	IV.	V.	VI.
4 hours ..	12°	46	36	—	55	60	45
20 ,, ..	11·3°	175	128	—	160	175	135
68 ,, ..	12°	544	442	—	455	522	416
2 hours ..	14°	75	50	12	36	28	23
18 ,, ..	12·5°	358	303	133	205	210	195
66 ,, ..	13°	1055	888	861	645	817	743

The ammonia produced in the reaction cannot, it is evident, be the cause of the diminution or of the acceleration already noticed, because where the diminution occurs, the ammonia present would increase the action, and where the increase occurs, it would occasion a decrease. Potash does augment the production of hydrogen, but this throws no light on the cause of the diminution, and only partially accounts for the great amount of reduction at the end of the reaction : for it appears from our experiments that the maximum amount of hydrogen obtainable per day from couples with water corresponding with those used, amounts to 24 milligrams. And leaving out of consideration the influence of the ammonia—which in general is a retarding one—the potash produced in the reaction might give 66 milligrams of hydrogen, whereas the reduction of the last day in Expt. I is equal to 107·2 milligrams above that of the first day, whilst in that of Expt. II it is 185·8 milligrams for the same quantity of couple.

This reduction to nitrite may be shown to an audience as follows :—

Pour a solution of nitre—about 10 per cent.—with enough copper sulphate to colour the liquid distinctly, on to some granulated zinc in a tap-funnel ; leave it for a few seconds, and then run off some of the liquid, when the green colour of copper nitrite will be evident. Drop the remainder of the liquid into some starch-solution with potassium iodide and acetic acid : the blue iodide of starch will be instantly formed.

The reaction may also be utilised as a test for nitrates. For this purpose add to about 5 c.c. of solution 12 drops of copper sulphate and four or five pieces of zinc foil ($1 \times \frac{1}{2}$ inch). Wait about three minutes, then pour the liquid, or a part of it, into about 5 c.c. of starch solution containing a little potassium iodide and acetic acid. A blue coloration forms at once, or in a second or two. By inverting the test-tube containing the test before pouring off, the liquid will be seen to

be green. Confirmation may be had by pouring some Nessler reagent into the completely decolorised solution. The reaction with starch can be readily and certainly obtained with 1 part of nitre in 500 of water, and the Nessler reaction with 1 part in 10,000.

Part II.

At least three views may be taken of the foregoing change :—

I. It may be considered that the zinc, augmented in its activity by contact with the copper, combines with the oxygen of the nitrate.

II. That the zinc and copper electrolyse the water present, and that the nascent hydrogen set free effects the reduction in the vicinity of the negative metal.

III. That the two metals electrolyse the nitrate of potassium, with formation of nitrate of zinc, the reduction being effected at the negative pole through the agency of the potassium.

The first view may be expressed by the following equation :—

$$KNO_3 + Zn = ZnO + KNO_2,$$
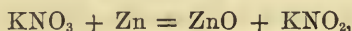
while the further action requires the intervention of water, with the following result :—

$$KNO_2 + 3Zn + 5H_2O = KHO + 3Zn(HO)_2 + NH_3.$$

Of course this may be brought about by the formation of intermediate compounds.

The second view may be represented thus—

$$(a.)\ Zn\ |\ OH_2\ |\ Cu = ZnO\ |\ H_2\ |\ Cu,$$
$$(b.)\ KNO_3 + H_2\ \ = H_2O + KNO_2,$$
$$(c.)\ KNO_2 + H_6\ \ = H_2O + NH_3 + KHO.$$

And the third view thus—

$$Zn\ |\ NO_3K\ |\ NO_3K\ |\ Cu = Zn(NO_3)_2\ |\ K_2\ |\ Cu.$$
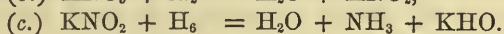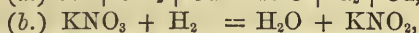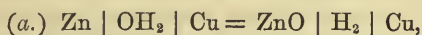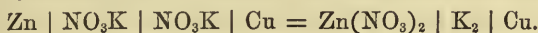
It may be conceived that this potassium is actually set free and at once acts upon the water, thus—

$$K_2 + 2H_2O = 2KHO + H_2\ ;$$
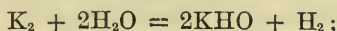
or other combinations of the elements present may be easily conceived to take place with the same final result.

The KHO and $Zn(NO_3)_2$ produced would of course react, with formation of zinc hydrate and potassium nitrate, so that the several changes at each cycle produce a molecule of hydrogen or its equivalent, which acts on nitre in accordance with equations b and c.

With reference to the first view, it was found that powdered zinc

and dry nitre, when heated together, detonate explosively, a quantity of gas—probably nitrogen—being produced, together with a solid, consisting of zinc oxide and potassium nitrite and oxide. And Schön-bein and Divers have shown that a solution of nitre is reduced by metals more positive than zinc to potassium nitrite and ammonia; but in this case it must be borne in mind that hydrogen is simultaneously produced by the decomposition of water.

Again, an experiment suggested itself which we hoped would assist in deciding between this and the second and third views. A boxwood cell was cut vertically into two equal parts, some pieces of parchment paper were placed between these, and the divisions of the cell held firmly together by a clamp. A solution of nitre was placed in each of the divisions, a strip of zinc being placed in one, a strip of platinum in the other. The strips were connected together by a metallic wire, and allowed to remain so for two or four days, the action being a feeble one. The general result of several experiments was, a little ammonia in each of the divisions; free potassium hydrate in the platinum one, none in the zinc; and about ten times less nitrite in the platinum than in the zinc division.

This great increase of nitrite in the zinc division would appear to lend material aid to the first view, which requires the reduction to take place by, and in the immediate vicinity of, the zinc plate. At this stage it occurred to us that this reduction might, after all, be due to a couple action, the negative element of such couple being the impurities in the zinc itself; and on trial, we found that similar zinc, when not connected with platinum, reduced nitre to almost the same extent as when metallically associated with that metal as described above. Moreover, we found that equal quantities of granulated redistilled zinc and commercial zinc placed in contact with equal volumes of nitre solution gave in equal times nitrite in the ratio $1 : 2\cdot7$. No deduction can therefore be drawn from the presence of the proportionately large amount of nitrite in the zinc division of the cell.

That an electric current traverses the nitre solution in the cell experiment, from the zinc to the platinum in the liquid, was ascertained by including a galvanometer in the circuit, which, in conjunction with the appearance of potassium hydrate in appreciable amount along with an excess of unaltered nitre in the platinum division, lends, we think, material aid to hypothesis III.

Whether hypothesis I or III be the more tenable may not be considered yet decided, but the results exhibited in the following table of a series of comparative experiments on the action of the couple on water, and on solutions of potassium nitrate and nitrite, certainly point to the untenability of II.

Employed for No. 1 KNO$_2$, 500 c.c. of ·922 per cent.
,,   ,, No. 2   ,,   481 ,, ,, ·956   ,,
,,   ,, No. 1 KNO$_3$, 435 ,, ,, 1·25   ,,
,,   ,, No. 2   ,,   462 ,, ,, 1·18   ,,

For comparison the total work done by the couples in the given times is expressed in milligrams of hydrogen.

Time in hours.	Water.		KNO$_2$.		KNO$_3$.	
	1.	2.	1.	2.	1.	2.
2	2	1 ·5	40 ·2	33 ·8	31 ·7	34 ·6
20	20 ·2	17 ·2	118	106	106	108
28	29 ·4	24 ·4	200	198	124	144
45	46	39	209	211	183	193
93	87	73	273	247	222	239
101	93	84	293	272	No observation	
117	108	96	—	309	234	247
141	132	116	—	—	237	243
148	136	120	—	—	296	—
165	153	134	—	—	331	369

It is evident that the nitre does not simply remain passive, and allow itself to be reduced by the hydrogen evolved from the direct decomposition of water by the couple, which hypothesis II requires: for were this the case, the reduction of the salt, at least at the beginning of the action, would be equivalent only to the hydrogen set free from the water couple alone, whereas the oxygen actually removed is equivalent to about 19 times that amount. It is noticeable that the first numbers given by the nitrite and the nitrate are nearly the same, and that in the respective columns of the salts they do not diverge much from one another for some time, which is of considerable interest, as showing that the ammonia and potassium hydrate, which must pour into the solution in the nitrite experiment from its very commencement, do not materially augment the action of the couple.

The weight of evidence certainly inclines to hypothesis III, which is to a great extent confirmed by the following experiments.

Electrolysis of Nitrate of Potassium.

I. A V-shaped tube was used, the bend being well plugged with fine asbestos. About 25 c.c. of a 5 per cent. solution of nitre were poured into each of the limbs. An amalgamated zinc plate 1·5 centimeters wide, connected by a wire with the platinum end of 4 Grove's cells, was immersed to the depth of one decimeter in one limb of the tube, a copper plate, of double the surface connected with the zinc end of the

battery, being placed in the other. The current was allowed to pass through the liquid for four hours. A trace only of gas escaped from the copper electrode, in the vicinity of which alkali was found immediately after making connection. A quantitative examination of the solutions in the respective limbs gave, in addition to the undecomposed nitre—

Zinc limb .... 0·3273 grams $Zn(NO_3)_2$

Copper limb ...... $\begin{cases} 0·197 & ,, & KHO \\ 0·0765 & ,, & KNO_2 \\ 0·00375 & ,, & NH_3. \end{cases}$

The amount of zinc nitrate was ascertained by precipitating the metal as carbonate, and calculating the oxide subsequently obtained as nitrate. Had zinc oxide been produced in this experiment and passed into solution, this method of analysis would give a quantity of nitrate greater than that actually present. The question therefore arose, does zinc oxide form in the experiment? and, if so, does it dissolve in a solution of nitre or zinc nitrate? We agitated zinc hydrate with nitre solution, also boiled the substances together. No zinc passed into solution. Small quantities of zinc hydrate were agitated with a solution of zinc nitrate. None disappeared. Schindler also states (*Gmelin*, v, 34) that zinc oxide when boiled with the nitrate does not dissolve. Again, zinc oxide was looked for on the zinc plate, and in the solution in its neighbourhood, during the action in this and subsequent experiments. Not a trace could be seen even when 20 Grove cells were employed. Every NH_3, therefore, represents 4 of the $Zn(NO_3)_2$ estimated as described, as seen by the equation :—

(*a.*) $4Zn \mid 8NO_3K \mid Cu = 4Zn(NO_3)_2 \mid K_8 \mid Cu$
(*b.*) $8K + 6H_2O + KNO_3 = 9KHO + NH_3,$
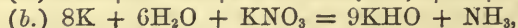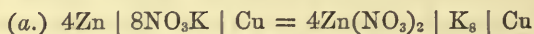
and every KNO_2 represents one of zinc nitrate, thus :—

(*c.*) $Zn \mid 2NO_3K \mid Cu = Zn(NO_3)_2 \mid K_2 \mid Cu$
(*d.*) $K_2 + H_2O + KNO_3 = KNO_2 + 2KHO.$
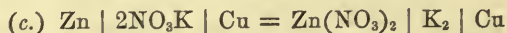
Calculating then the ammonia and nitrite found in the copper limb into zinc nitrate, according to these equations, we obtain 0·337 gram of that salt, which is 0·01 in excess of that found in the zinc limb by analysis, and equal to 0·0043 gram of zinc oxide—a quantity which might have formed on the zinc plate and yet have escaped detection.

II. A 3 per cent. solution was used in this experiment. In other respects it was similar to the last.

Found in zinc limb........ 0·2596 gram $Zn(NO_3)_2$

Copper limb .... $\begin{cases} 0·1366 & ,, & KHO \\ 0·05355 & ,, & KNO_2 \\ 0·00294 & ,, & NH_3, \end{cases}$

the two latter of which products give 0·2501 gram of $Zn(NO_3)_2$, which is slightly less than that found.

III. A 3 per cent. solution was used, the current passed for three hours. In other respects similar to I and II.

Found in zinc limb ......   0·1645 gram $Zn(NO_3)_2$

Found in copper limb .... $\begin{cases} 0·0942 & ,, & KHO \\ 0·03706 & ,, & KNO_2 \\ 0·00157 & ,, & NH_3, \end{cases}$

the latter of which are equal to 0·1524 gram of $Zn(NO_3)_2$, which is again below that actually found by analysis. We may therefore conclude, that in these experiments nitre alone suffered electrolytic decomposition.

One other point is worthy of notice here. In the experiments just described not a trace of nitrite or ammonia could be detected in the zinc limb, which we think finally disposes of hypothesis I, because, if the zinc electrode, when charged with positive electricity, fails to reduce nitre in its immediate vicinity, the zinc of the couple so charged might reasonably be expected not to act. Of course we do not contend that in these electrolytic experiments we have identically the same conditions as obtain in the couple decompositions, but that we have a similarity of condition no one can doubt.

Potassium Chlorate.

Action of Couple.—Thorpe (*Chem. Soc. Jour.*, 1873, 547) has shown that our couple reduces potassium chlorate to chloride.* We have studied this reaction with the view of ascertaining whether chlorite or hypochlorite forms during the passage of the salt to chloride. So far as we have been able to determine, these intermediate compounds are not produced. It may be remarked that the chlorate is more rapidly reduced than the nitrate. Thus in a comparative trial, employing equivalent quantities of the two salts, and similar couples, the hydrogen equivalent to the reduction was such as to give the following ratios :—

	Nitrate.	Chlorate.			Nitrate.	Chlorate.
1st hour	1 :	1·15		5th hour	1 :	3·86
3rd ,, ...	1 :	2·50		21st ,, ...	1 :	2·97

Electrolysis.—As soon as an aqueous solution of this salt begins to be

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* This reaction may be utilised for the detection of small quantities of chlorates. Add some twelve drops of strong cupric sulphate to about 5 c.c. of solution, then 3 or 4 pieces of zinc foil about 1 inch × ½, boil for a minute or two, or wait till solution is decolorised, filter if necessary and add to the filtrate a few drops of nitric acid and nitrate of silver. A very minute quantity can thus be detected.

electrolysed by an external battery, alkali may at once be detected close
to the negative electrode, but instead of the potassium chlorate being
reduced to chloride, the greater part of the hydrogen escapes as gas.
Employing the arrangement as used for the nitre solution, a current of
four cells gave in four hours 0·00244 gram of potassium chloride in the
copper limb, and 0·4775 of zinc chlorate in the zinc limb. Calculating
the equivalent of the potassium chloride found according to the equa-
tions—

$$(a.) \quad 3Zn \mid 6ClO_3K \mid Cu = 3Zn(ClO_3)_2 \mid K_6 \mid Cu.$$
$$(b.) \quad K_6 + 3H_2O + KClO_3 = 6KHO + KCl.$$
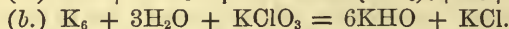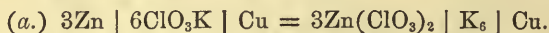
we get only 0·0228 of zinc chlorate. Therefore 95·2 per cent. of the
hydrogen formed in the experiment passed through the liquid.

About four years ago it was pointed out by one of us (*Chem. Soc.
Jour.*, 1874, p. 415) that finely divided copper, immersed in acidulated
water, agglomerated—that is, formed into more or less coherent lumps—
when subjected to the action of nascent hydrogen : also that the finely
divided particles of palladium and platinum—metals known to con-
dense hydrogen, agglomerated, when similarly treated ; further, that
the agglomerated copper, palladium, &c., deglomerated when treated
with nascent oxygen:—from all which it was inferred that the copper of
the couple was also capable in a slight degree of absorbing hydrogen
gas.

Graham has shown that occluded hydrogen is a somewhat powerful
reducing agent ; and to us, having traced the reducing action of the
couple in some way to hydrogen, it appeared of exceptional interest to
ascertain whether hydrogen associated with the finely divided copper
of the couple could reduce nitre to nitrite. With this object some
copper was precipitated by immersion of a zinc plate in a 2 per cent.
solution of copper sulphate till decolorised. As has been already
pointed out, the deposit thus obtained contains metallic zinc. To
remove this and to charge the residual metal with hydrogen, dilute
sulphuric acid was added, which immediately brought about a power-
ful agglomeration of the copper. After standing with the acid for
about an hour, with occasional shaking, the metal was well washed,
and some nitre solution added, when almost immediately the whole
deglomerated, shrinking in volume to about a quarter. The solu-
tion contained a small quantity of both ammonia and potassium nitrite,
which was found equal per 100 grams of copper to 4 milligrams of
hydrogen.

For the next trial copper was deposited as before, but from a 1 per
cent. solution of the sulphate. The deposit was treated with succes-
sive portions of copper sulphate for some hours. The residual metal
was then divided into two portions. To one, some nitre solution was
added ; to the other some dilute sulphuric acid. This after shaking

was poured into a dish, at the bottom of which was a sheet of platinum in connection with the zinc end of 4 Grove's cells. As soon as the metal had settled, the positive electrode was dipped into the acidulated water near its surface. The copper slowly agglomerated without material change in colour, and in about 30 minutes hydrogen was freely escaping from it. After washing this a few times, and neutralising with potassium hydrate, a quantity of nitre was added equal to that added to the first portion. Ammonia and nitrite were found in both. The portion not treated with hydrogen gave, per 100 grams of copper, 3·5 milligrams of hydrogen, the agglomerated giving, for a similar quantity of copper, 8 milligrams of hydrogen. Zinc was also found in small quantity in both, but the non-agglomerated contained at least four times the amount of that present in the hydrogenised. Another effort was made to get the finely divided copper free from zinc. Some deposit, obtained as in the last experiment, was digested, with occasional shaking, for three days with about 5 per cent. solution of copper sulphate. It was then well washed and divided into two parts. To one some nitre was added. The other, previously to the addition of an equal quantity of this salt, was digested with dilute sulphuric acid for an hour, washed, again mixed with dilute acid, hydrogenised for two hours, and the adhering acid neutralised with potash. The non-hydrogenised contained nitrite and ammonia, equal, per 100 grams of copper, to 2·7 milligrams of hydrogen. The hydrogenised portion, for the same amount of copper, contained 19·3 milligrams of hydrogen. Both portions still contained a small quantity of zinc—whether as metal or oxide, or both, there is no means of determining. It is certain that some oxide existed in the portions not treated with acid, and some zinc may have existed as metal, but completely protected by a covering of copper. The reduction effected by the non-hydrogenised portions may also be due to hydrogen occluded during their preparation, but we cannot speak with certainty about it, in consequence of the possible presence of metallic zinc. There can be no doubt, however, that the finely divided copper of our couple does condense hydrogen, and when in this condition reduces nitre to nitrite and ammonia.

Two facts which appeared difficult to reconcile, now appear intelligible enough: the one, that the couple reduces the chlorate in the cold without the least escape of hydrogen; the other, that in the ordinary electrolysis of the chlorate, nearly the whole of this gas escapes without reducing the salt. The reason is obvious. In the first case the hydrogen is probably wholly occluded the moment it is set free, while in the other, only a small quantity of the gas is condensed by the negative plate.

Taking into consideration all the facts brought out by this inquiry, we consider it proved that—

a. The action of the copper-zinc couple on these oxy-salts is of an electrolytic nature.

b. The negative radicle combines with the zinc, whilst the positive radicle, or its equivalent of hydrogen from decomposed water, is set free against the copper crystals.

c. The reduction and hydrogenisation of the salt take place in the immediate vicinity of the negative metal.

We also think it probable that hydrogen is actually set free against the copper, but is condensed by the finely divided metal, and in that condition does its work of reduction and hydrogenisation.

Of course the resulting zinc compound and the alkaline hydrate decompose one another, producing the original salt and zinc hydrate.

Ammonium Nitrate.

It may be assumed that this action of the couple is a general one, true not only of nitre, but of all nitrates containing metals which decompose water at the ordinary temperature. Ammonium nitrate, though not strictly belonging to this class of bodies, should, according to what is known of the electrolysis of ammonium salts, and to the views just enunciated, give off a fourth of the hydrogen in its positive radicle when its solution is subjected to the action of the couple; and since it is very probable that the real reducer in these actions is hydrogen, it naturally occurred to us that this salt ought not to form an exception to the above generalisation. But to place the matter beyond doubt, we instituted a few additional experiments.

A qualitative experiment with the couple showed at once that both nitrite and ammonia were produced, but not hyponitrite.

We give the details of a quantitative trial:—410 c.c. of about 1·2 per cent. solution of ammonium nitrate were added to the usual quantity of couple (temp. 15° C.), and the ammonia and nitrate estimated. Subjoined are the results reckoned for 100 parts of solution:—

Time.	NH_3.	NH_4NO_2.	Equivalent to NH_4NO_3.	Work done each hour expressed in milligrams of Hydrogen.
1 hour..........	0·039	0·209	0·4445	100
4 hours	0·114	0·185	0·767	45·5
11 „	0·179	0·159	1·04	16·4
23 „	0·243	Nil	1·143	7·8

The action of heat on a solution of ammonium nitrite resolves it, as is well known, into nitrogen and water, from which it was inferred

that were this reduction attempted at or near the boiling point of the solution of the nitrate, the nitrite as quickly as produced would be decomposed in like manner. On trial, gas was evolved, but this proved to be mainly nitric oxide, which gas Thorpe had noticed on boiling solution of ammonium nitrate with the couple (*Chem. Soc. Journal*, 1873, p. 544). The amount of this oxide of nitrogen we found increased with the strength of the nitrate solution. Thus with strengths of 20, 10 and 5 per cent. and an excess of couple, the nitric oxide was 8·5, 6 and 3 respectively. In the cold the nitrate, even in solution of 20 per cent., was completely reduced to ammonia in about 24 hours without the escape of nitrogen free or combined. We might suggest therefore that, in estimating unknown nitrates by Thorpe's process, it would be well to allow the couple to remain in contact with the nitrate solution for at least 24 hours prior to distillation.

ANALOGIES BETWEEN THE ACTION OF THE COPPER-ZINC COUPLE AND OF OCCLUDED AND NASCENT HYDROGEN.

By J. H. GLADSTONE, Pres. C.S., F.R.S., and ALFRED TRIBE, Lecturer on Chemistry in Dulwich College.

WE have recently pointed out (this volume, page 139) that finely divided copper charged with hydrogen converts nitre into potassium nitrite and ammonia. Hydrogen in association with the same metal, we have since found, reduces potassium chlorate to the chloride. These results are in perfect agreement with those obtained by the action of the copper-zinc couple on solutions of the same salts.

On thinking further of this matter, it appeared to us that if copper-hydrogen was capable of effecting such a reduction, the platinum or palladium combinations, in which occluded hydrogen enters in much larger quantity, ought to do it with still greater facility. It also appeared desirable to study the action of the copper-zinc couple on other compounds side by side with that of occluded hydrogen, and especially to ascertain whether a metal is absolutely necessary, or whether hydrogen occluded by carbon would act in the same manner.

Our attention was also naturally drawn to that condition of hydrogen which is usually denominated nascent, and to which special power is attributed. It became interesting, therefore, to see whether the reactions usually attributed to nascent hydrogen, such as the reduction of nitrobenzene, of ferricyanide of potassium, of sulphurous acid, of arsenious acid, and of blue indigo, could not be effected under circumstances in which the hydrogen was no longer nascent.

Copper-Zinc Couple.

We find that beside the many reductions previously described, our copper-zinc couple, in presence of water, converts nitrobenzene into

aniline, a reaction which may be utilised for the detection of small quantities of the former substance;[*] liberates sulphur from sulphurous acid, without, however, producing sulphuretted hydrogen; and converts blue into white indigo in presence of weak alkali.

Palladium-Hydrogen.

A quantity of palladium black was precipitated by the action of an alkaline formate on palladium nitrate, and after washing with water and drying at 100°, it was heated at the same temperature for about 30 minutes, in a current of dry hydrogen, and afterwards slowly cooled in the same gas.

Potassium Nitrate.—An experiment by Böttger showed that nitrite was produced by the action of palladium-hydrogen on this salt. We find that both nitrite and ammonia are quickly produced, but no hyponitrite. A quantitative trial gave the following results, when 100 c.c. of a 5 per cent. solution of nitre were poured at the ordinary temperature on 30 grams of the palladium-hydrogen. Almost immediately after adding the solution, it was noticed to be sensibly warm. The temperature was kept from rising by immersing the flask in water (18°) for 10 minutes.

Time.	Temp.	Quantities in grams.		Hydrogen required by the KNO_2 and NH_3 in grams.	KNO_3 decomposed.
		KNO_2.	NH_3.		
10 minutes.	19° C.	·154	·0094	·0081	·239
30 ,,	24°	·363	·0375	·0262	·657
60 ,,	32°	·276	·092	·049	·876
90 ,,	34°	·191	·143	·072	1·07
120 ,,	33°	·115	·204	·099	1·35
22 hours.	19°	Nil	·222	·107	1·351

The general result here is the same as with the couple:—no production of hyponitrite, but ammonia and nitrite at the beginning of the action, and the subsequent simultaneous decomposition of potassium nitrate and nitrite.

[*] Add some twelve drops of strong copper sulphate solution to three or four pieces of zinc foil (1 inch × ½) in about 5 c.c. of water; wait till the liquid is nearly or completely decolorised; pour off the zinc sulphate solution; and wash the conjoined metals three or four times with water. Now add to this couple the nitrobenzene in solution or in suspension in water; heat nearly to boiling for about two minutes; filter if necessary; cool; and add, drop by drop, a solution of bleaching powder. In this way the violet coloration indicative of aniline may be most distinctly obtained in 5 c.c. of an aqueous solution of nitrobenzene containing ·5 gram in 1000 c.c. of water.

Potassium Chlorate.—The couple reduces this salt to chloride without producing any of the intermediate oxy-compounds. The same result is brought about by palladium-hydrogen. We subjoin the results of an experiment for which 30 grams of the hydrogenised metal, and 100 c.c. of a 5·6 per cent. solution of potassium chlorate were employed. The temperature of the solution, on mixing, rose more rapidly than in the corresponding nitre experiment. The flask was immersed in water for 10 minutes.

Time.	Temp.	KCl produced in grams.	Hydrogen required.
10 minutes.	19° C.	0·751	·0605
30 ,,	33°	1·258	·1013
60 ,,	29°	1·429	·1152
90 ,,	27°	1·501	·1209
120 ,,	—	1·528	·123
22 hours.	—	1·672	·1347

The amount of hydrogen used up in this experiment is some seven times greater for the first 10 minutes than that oxidised by the equivalent nitre solution in the same time. The couple also reduces the chlorate more rapidly than it does the nitrate.

30 grams of the same preparation of palladium-black hydrogenised were heated to redness, when 0·130 gram of hydrogen was liberated. Thus it would appear that the solution of a reducible oxy-salt can extract practically the whole of the hydrogen stored up by the metal, or at least all that can be driven off at a red heat at the ordinary pressure.

Like the copper-zinc couple, palladium-hydrogen is incapable of reducing the potassium perchlorate; but it easily reduces nitrobenzene in aqueous alcohol to aniline; changes blue to white indigo in presence of weak potash-solution; converts solution of sulphurous acid into sulphuretted hydrogen; and reduces a solution of arsenious acid to metal, without, however, the production of arsenuretted hydrogen.

Platinum-Hydrogen.

Some platinum-black was prepared by the method employed for the preparation of the palladium. After precipitation the metal was boiled with a solution of potash until free from ammonia; then, after thorough washing with water, treated with hydrochloric acid, washed until free from acid, dried at 100°, and hydrogenised in like manner to the palladium.

Potassium Chlorate.—120 c.c. of a 5 per cent. solution of this salt were added to 25 grams of the prepared metal. Immediately chlorate

was reduced, corresponding to ·0165 gram of chloride; in 6 minutes, to ·0472 gram; and in 18 hours (when, and probably long prior to which, the action was over), to ·0719 gram.

Potassium Nitrate.—Our experience here is somewhat curious. Some solution was found to be free from ammonia after being in contact with the conjoint elements for some hours. In another trial ammonia was detected in quantity soon after putting the substances together, but in a few hours the solution gave but a very slight coloration with the Nessler reagent.

A quantitative experiment, employing 30 grams of the hydrogenised metal, and 100 c.c. of a 5 per cent. solution of nitre, gave :—

Immediately........	·006 per cent. ammonia.	
2 minutes	·0075 ,,	,,
7 ,, ...	·0030 ,,	,,
37 ,, ...	·00035 ,,	,,
2 hours	trace of ammonia.	

Another similar experiment, but with a different specimen of the platinum-hydrogen, gave :—

Immediately........	·0032 per cent. ammonia.	
10 minutes	·002 ,,	,,
37 ,, ...	·0014 ,,	,,
20 hours	·0004 ,,	,,

Nitrite could not be detected in any of the stages of either of these experiments.

But why does the ammonia pass from solution? The metal being hydrogenised precludes the possibility of the presence of oxygen, which might under the circumstances get rid of the ammonia by oxidation. Is it absorbed by the finely divided metal? The platinum of the first experiment was washed with water, until the washings were free from anything but a mere trace of ammonia, then boiled with hydrochloric acid. Some metal dissolved, owing, perhaps, to adhering nitrate, and the solution, after the removal of this by potash, gave a copious precipitate with the Nessler reagent. The metal of the second experiment was likewise thoroughly washed, then boiled with caustic potash, which set free ·0017 gram of ammonia. The quantity of this substance, taken out in the portions of liquid used for the estimations, amounted to ·0012, which, added to that evolved from the metal by potash, approaches the ·0032 gram found immediately after pouring on the solution. Platinum then abstracts ammonia from solution, which fully accounts for its disappearance in the reaction.

It would appear from these results, that hydrogen associated with platinum is much more energetic than when it is associated with

palladium, although the latter metal fixes a much greater quantity of the gas. This is seen in the amounts of chlorate reduced in the time experiments by the platinum-hydrogen and the palladium-hydrogen respectively. Thus the hydrogen of the palladium-hydrogen reduced in 10 minutes 45 per cent. of the possible quantity, whereas the hydrogen of the platinum-hydrogen reduced in 4 minutes 65·6 per cent. Again, the fact that platinum-hydrogen apparently reduces by one operation the nitrate to ammonia, points to the same conclusion, although there can be but little doubt that this change takes place through the nitrite—in fact, distinct though slight evidence of this was noticed with another preparation of platinum-hydrogen.

In addition we find that platinum-hydrogen readily reduces ferri- to ferro-cyanide, and like palladium-hydrogen converts a solution of arsenious acid to metallic arsenic, without the production of arsenuretted hydrogen. With nitrobenzene, however, it produces, not aniline, but a substance which dissolves in alcohol to a red solution, probably azobenzene, and although it reduces a solution of sulphurous acid, it gives no sulphuretted hydrogen.

Carbon-Hydrogen.

Hunter has shown that cocoa-nut charcoal is more absorptive for gases than other kinds of vegetable charcoal. We therefore selected it for our experiments. The first quantitative trial was made by pouring 100 c.c. of a 5 per cent. solution of potassic chlorate on 40 grams of the powdered carbon, hydrogenised by heating to redness and subsequent cooling in a current of hydrogen. Corresponding volumes of solution of potassium chlorate and of water respectively were poured at the same time on similar quantities of the untreated charcoal. In each case the materials remained together for 20 hours at the ordinary temperature (about 18°), when the chloride was estimated by precipitation with silver nitrate, after acidifying with nitric acid. The silver chloride obtained would correspond with 4·2 milligrams of hydrogen for the hydrogenised; 3·2 for the non-hydrogenised with solution of potassium chlorate; and 2·4 for the non-hydrogenised and water. The chloride found in the experiment with water alone represents of course the amount extracted from the charcoal; deducting this from that found in the first experiment, it is seen that the hydrogenised carbon exerts an appreciable reducing action on the chlorate. The difference noticeable between the non-hydrogenised carbon with chlorate and that with water alone may possibly result from the presence of occluded carbonic oxide. In the hope of removing this source of error, and also the chloride and any conceivable traces of iron or carbide, which would doubtless form reducing couples with the

carbon, we digested the powdered charcoal for 20 hours at the ordinary temperature, with a considerable quantity of nitric acid of about 30 per cent. The substances were then heated together to about 50°, after which the carbon was washed with hot water until the washings were free from chloride and acid, and finally dried at about 200°.

40 grams of this carbon were hydrogenised as described, and poured into a flask containing 100 c.c. of potassium chlorate solution at about 0°, the object of the lower temperature being to give the hydrogen greater time in which to act, as we had noticed that, at the ordinary temperature the liquid physically replaces the gas somewhat quickly. The materials remained together for about an hour at 0°, and for some hours at the ordinary temperature. A similar experiment was made with the purified charcoal non-hydrogenised. The silver chloride obtained for the hydrogenised corresponded to 23 milligrams of hydrogen, and only 0·3 for the non-hydrogenised.

Common wood charcoal purified with nitric acid, as described, gave for 40 grams of carbon-hydrogen, chloride corresponding with 2·5 milligrams of hydrogen, whilst a similar quantity of non-hydrogenised gave but the merest trace.

Further proof of this reduction being occasioned by occluded hydrogen is furnished by the fact that carbon-hydrogen loses some of this power on exposure to the air, resembling in this respect platinum-hydrogen and palladium-hydrogen. In an experiment employing 40 grams of hydrogenised carbon of the same specimen as that used in the first of these last two experiments, which had been warmed and cooled in air previously to being put in contact with the chlorate solution, chloride was obtained corresponding with only ·6 of a milligram of hydrogen, from which it appears that the air removed by oxidation about a fourth of the active agent.

Carbon-hydrogen has no action on a solution of nitre, but easily reduces a solution of ferri- to ferro-cyanide of potassium.

Conclusions.

It is evident from these experiments that there is a close analogy between some actions of the copper-zinc couple, of occluded hydrogen, and of the so-called nascent hydrogen.

As to the copper-zinc couple, we conceive that these fresh experiments very strongly corroborate the view which we thought probable in our last paper, that its great power of reduction and hydrogenisation depends on the absorption of hydrogen by the finely divided metal.

As to the hydrogen occluded in metals, it is well known that this does not form any very strongly marked chemical compounds. It is

true that Graham looked upon the palladium combination as an alloy of hydrogen, and Favre, from his thermometric observations, came to the conclusion that it was a definite chemical compound; but other observers have drawn opposite deductions, and our experiments clearly show a close analogy between the chemical reactions of palladium-hydrogen and the combinations of hydrogen with platinum and copper, and even with carbon.

It must, however, be borne in mind that our experiments, while they show a close similarity between the action of hydrogen as occluded by the several elements, show also certain differences, as set out in the annexed table.

Substances employed.	Substances produced by				
	Copper-zinc couple.	Palladium-hydrogen.	Platinum-hydrogen.	Copper-hydrogen.	Carbon-hydrogen.
$KClO_3$, aqueous solution	Chloride*	Chloride	Chloride	Chloride	Chloride
KNO_3, aqueous solution	Nitrite and ammonia*	Nitrite† and ammonia	Nitrite (?) and ammonia	Nitrite and ammonia	Nil.
K_3Cy_6Fe, aqueous solution	Ferrocyanide	Ferrocyanide‡	Ferrocyanide	—	Ferro-cyanide
$C_6H_5NO_2$, aqueous or alcoholic solution	Aniline	Aniline	Azobenzene	—	—
Indigo, with weak solution of potash	White indigo	White indigo	—	—	—
H_2SO_3, aqueous solution	Sulphur	Sulphuretted hydrogen	Sulphur (probably)	—	—
As_2O_3, aqueous solution	Arsenuretted hydrogen	Metallic arsenic	Metallic arsenic	—	—

At least three views may be taken of these reactions—

1. That the energy of the hydrogen is increased by its association with a more negative element. This explanation will apply to the carbon combination as well as the others, for the specimens of cocoa-nut and ordinary wood charcoal were found to conduct electricity freely. Upon this view we should expect that the power of these combinations would increase with the electro-negative character of the

* Thorpe.   † Böttger.   ‡ Graham.

element with which the hydrogen is associated.   This seems scarcely borne out by our results, but there are many points that require consideration before this can be fully decided.

2. That the atomic condition of occluded hydrogen differs from that of ordinary hydrogen, the variations shown in the experiments being ascribable to different atomic aggregation.

3. That the increased power of the hydrogen is due to its condensed condition, while the observed differences between the actions of the different combinations result from variations in this respect, and perhaps also from the more or less firm hold which the metal has upon the gas.

The above chemical changes are effected more or less perfectly by nascent hydrogen.   But this hydrogen in every case is set free in contact with, or in very close proximity to a metal, which in virtue of the power known to be possessed by such solids very probably condenses and fixes some of this gas.   It may therefore be conceived that the activity of the hydrogen under these circumstances is but the consequence of its intimate association with the metals, or, in other words, of its being in the occluded condition.

RESEARCHES ON THE ACTION OF THE COPPER-ZINC COUPLE ON ORGANIC BODIES.

Part IX. *Preparation of Zinc-Methyl.*

By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, Lecturer on Chemistry in Dulwich College.

In a previous communication (*Chem. Soc. J.*, 1873, page 682) we stated that methyl iodide is but slightly acted upon by the copper-zinc couple, at its boiling point; indeed, so slightly that we did not look upon this as a practical method of preparing the zinc-compound. But from theoretical considerations relative to the formation of the C_nH_{2n+2} hydrocarbons, we arrived at the opinion that this iodide would be slowly acted upon by the zinc of the couple, even at the ordinary temperature.

An examination of this forecast was made by taking a number of dry couples prepared from half a meter of foil as described in this Journal 1877, i, 567, pouring on them 5 c.c. (11 grams) of methyl iodide, well corking the flasks containing the materials, and making daily observations of any changes. In a day or two some white grains were noticeable intermingled with the couple, and adhering to the sides of the vessels, after which no further change could be detected for some time, when it was observed that the liquid was somewhat yellow, and had diminished in quantity. This apparent absorption of liquid continued, and almost as soon as it appeared complete, crystalline plates were seen studding the surface of the uppermost points of the couples, which went on increasing until the whole appeared one uniform beautifully crystalline mass. The times varied for the first and second parts of this reaction, and the whole particulars are set out in the following table :—

Experiment.	Mean temperature.	First signs of crystallisation.	Completion of action.
I.	18° C.	34 days	36 days
II.	„	29 „	31 „
III.	„	43 „	45 „
IV.	„	32 „	36 „
V.	20° C.	37 „	39 „
VI.	„	39 „	43 „
VII.	22° C.	28 „	30 „
VIII.	„	29 „	30 „

Zinc Methiodide.

On removing the corks of the flasks, a slight outrush of gas took place, followed immediately by white fumes within the vessels. The gas which escaped burnt when ignited, with a bluish flame, and it doubtless consisted of zinc-methyl, saturating the nitrogen of the air originally present. From the mode of formation of the crystalline body, and the absence of liquid or gaseous products, it can scarcely be other than the methyl analogue of Frankland's zinc ethiodide; and, from analogy, it might be expected to split up by heat into zinc iodide and zinc-methyl, zinc iodide, zinc, and di-methyl, or into a mixture of these several substances.

A cork with two tubes was fitted into one of the flasks containing the crystalline product from 5 c.c. of the iodide; one of the tubes was connected with a dry hydrogen supply; the other with a condenser with a fitted and weighed receiver. The gas, on passing through the apparatus for a few minutes, was found to be burning with a bluish flame, indicating the presence of zinc. The current of hydrogen was now stopped, and the flask slowly heated from the melting point of the paraffin bath to 100° C. At about 60° a perfectly clear and colourless liquid began to distil; in 15 minutes it ceased. The distillate weighed 2·7 grams. It was very mobile, had a powerful odour, was free from iodine, and very spontaneously inflammable; in fact, had all the properties ascribed by Frankland to zinc-methyl. The residue in the flask was nearly white, and consisted of zinc iodide. The 2·7 grams corresponds with 72 per cent. of the theoretical quantity, which, when we remember that it is less by that which necessarily adhered to the tubule of the condenser, &c., represents pretty closely the possible yield.

Progress of the Action.

Information as to the rate at which this chemical change takes place appeared very desirable. It was obtained by pouring 5 c.c. of the methyl iodide (at the summer temperature) on to each of five couples made as much alike as we could make them, and estimating the action by distilling the zinc-methyl from the product at the end of the first week in one, at the end of the second week in another, and so on. The results are tabulated below :—

Time.	$(CH_3)_2Zn.$
7 days	1·387 grams.
14 ,,	2·063 ,,
21 ,,	2·344 ,,
28 ,,	2·73 ,,
31 ,,	3·72 ,,

Signs of crystallisation were noticeable only in the last of these couples, and that on the twenty-ninth day. It appears therefore that, although the action probably starts with comparative energy, the methiodide crystallises and perhaps forms only when the whole of the methylic iodide has disappeared. The methiodide is, in fact, very soluble in methylic iodide.

Effect of Temperature and Time.

As already stated, the couple, when boiled with methyl iodide, decomposes it but slowly; but to obtain definite knowledge on this point, we boiled 5 c.c. of the iodide with the usual quantity of couple for 6 hours, and in another experiment for 22 hours. In the 6 hours the equivalent of 0·945 gram of zinc methyl formed, and in the 22 hours 1·4 grams.

The augmented temperature, as was to be expected, expedites the action, but it may be observed that at this higher temperature, as well as at the lower one, the formation of zinc-methiodide takes place in a rapidly-diminishing ratio with regard to time, even when all allowance is made for the diminishing amounts of liquid and zinc. Experiments were made on this point.
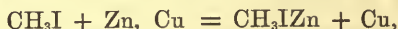
Effect of Quantity of Couple.

5 c.c. of the iodide were added at the ordinary temperature to twice the usual quantity of couple, when the action was found to be complete in three days; and when three times the quantity of couple was used and the same quantity of iodide, the action was over in one day; from which it would appear that the time required to bring about the decomposition of a given quantity of this iodide becomes 12 times less by doubling the amount of couple, and 36 times less by trebling it. We can only therefore attribute the rapidly-decreasing action as time advances to the interference of the zinc methiodide.
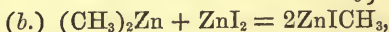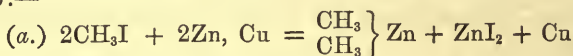
To study still more completely the changes involved, and in fact to analyse the crystalline body, the following experiment was made :—A flask containing the methiodide from 11·2 grams of methyl iodide, and the apparatus to which it was connected, were freed from air by dry carbonic anhydride, and the methiodide was decomposed in a current of this gas by heating up to 100°C. The zinc-methyl, as it was set free, was passed into dilute sulphuric acid, and the zinc therein was estimated as oxide. It weighed 2·934 grams, equivalent to 3·44 grams of zinc-methyl. The gas resulting from the decomposition of the volatile zinc-compound was collected over a solution of caustic potash. It measured 1,677 c.c. (corrected), and burnt with a somewhat luminous flame, at the same time depositing a small quantity of a yellowish-red substance. After standing, however, over water for a day, it burnt with an almost

colourless flame without the separation of any solid body, and from the quantity collected, and from what is known of the decomposition-products of zinc-methyl by water, there can be no doubt that it was pure, or nearly pure, marsh-gas. Now the 11·2 grams of methyl iodide could yield theoretically 3·75 grams of zinc-methyl, which, in presence of water, would give 1,764 c.c. of marsh-gas and 3·198 grams of zinc oxide, numbers which but very slightly exceed our experimental ones.

It appears then from this inquiry, that the action of our couple on iodide of methyl at the ordinary temperature is to build up zinc methiodide only;[*] whether in one stage, thus :—

$$CH_3I + Zn, Cu = CH_3IZn + Cu,$$

or in two :—

(a.) $2CH_3I + 2Zn, Cu = \left.{CH_3 \atop CH_3}\right\} Zn + ZnI_2 + Cu$

(b.) $(CH_3)_2Zn + ZnI_2 = 2ZnICH_3,$

is open to conjecture; and that this methiodide splits up very readily by heat, without fusing, into zinc iodide and zinc methyl, thus :—

$$2ZnICH_3 = ZnI_2 + Zn(CH_3)_2.$$
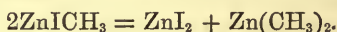
The methiodide is also decomposed by light, the white lustrous crystals becoming dark grey or black, probably from the separation of metallic zinc.

On starting this work, we placed 5 c.c. of methyl iodide in contact with the same quantity of zinc foil as has been employed for the couples used in these experiments. The surface of the metal became tarnished, but no signs of the methiodide appeared; and on opening the flask more than seven months afterwards, only a doubtful trace of any zinc-compound was found.

This investigation specially illustrates the value of our couple in bringing about, at a low temperature, a chemical change which can be brought about by its more positive element, only at such a temperature and under such conditions, as occasion the formation of secondary products. It has also furnished a perfect and really simple method of preparing Frankland's most valuable reagent, zinc-methyl: for in the last experiment described the yield of this substance amounts to 91·7 per cent. of the possible quantity, and in another, the results of which are given on the last line of page 108, to 99·2 per cent.

* In two instances out of about 30, the thin closed flasks containing the couple and iodide burst before the action was complete, which we are disposed to attribute to the accidental presence of moisture, giving rise to marsh-gas. All chance of bursting may be prevented by employing a Bunsen valve.

INVESTIGATIONS INTO THE ACTION OF SUBSTANCES IN THE NASCENT AND OCCLUDED CONDITIONS. HYDROGEN (CONTINUED).

By J. H. GLADSTONE, Pres. C.S., F.R.S., and ALFRED TRIBE, Lecturer on Chemistry in Dulwich College.

FROM our recent study of the behaviour of nascent and occluded hydrogen (*Chem. Soc. Trans.*, 1878, 306) we arrived at the opinion that these hitherto supposed different states of the element are very closely related, if not identical—that, in fact, the activity of the so-called nascent hydrogen is only the consequence of its intimate association with the metals employed to bring about the liberation of the element.

To test this conclusion still further, we determined to examine the action of nascent and occluded hydrogen on other bodies. The two acids, nitric and sulphuric, presented themselves to our mind more especially, because the results, whether they strengthened our hypothesis or not, would certainly assist in the elucidation of the chemistry of the action of metals upon these compounds.

Nascent Hydrogen and Nitric Acid.

The usual way of preparing nascent hydrogen is by acting on a metal by means of an acid, and the first idea might be that the action of nitric acid on zinc or some other metal would itself furnish the body upon which we intended to experiment. But a moment's reflection will show that the nitric acid in attacking a metal can only generate hydrogen by becoming itself a nitrate, and thus introducing a third body into the reaction, while every chemist knows that the nitric acid itself is actually more or less deoxidised; and how far this is dependent on, or independent of, nascent hydrogen, it is impossible to say. There seemed, in fact, to be only one source of hydrogen which was unexceptionable, that from the electrolysis of the acid itself. This electrolytic hydrogen is pre-eminently in a nascent condition, and it does not matter for our purpose whether we suppose that is the HNO_3 or the accompanying H_2O that primarily suffers decomposition.

We are not without former experiments on this subject. Faraday (*Phil. Trans.*, 1834) taught that in the electrolysis of very strong nitric acid no free hydrogen appeared at the cathode, but nitrous acid, and apparently, after some time, nitric oxide; further, that when the strong acid was mixed with an equal or greater bulk of water, hydrogen alone appeared, varying in quantity with the strength of the

acid or voltaic current, but equivalent to the oxygen at the anode.
Bourgoin (*J. Pharm.* [4], **13**, 266—270), who has more recently (1871)
investigated this subject, finds, like Faraday, that the strongest acid
gives no free hydrogen at the cathode, but that hydrogen alone ap-
pears there only when very dilute acid is employed. When acids of
the strengths 5·2 and 14·6 per cent. respectively were used, hydrogen
only was set free at the beginning of the action; nitrogen subse-
quently made its appearance, and also ammonia, but these substances
are most probably not produced by the action of hydrogen on nitric
acid, but are secondary or tertiary products of this action.

It would appear, then, that electrolytic or so-called nascent hydrogen
reduces strong nitric acid, but only imperfectly, or not at all, when
diluted with an equal bulk or more of water. But if the oxidation of
the freed hydrogen in this action results from its being in the occluded
condition, the reduction of the acid would depend upon the strength
only in so far as this facilitated the de-occlusion of the hydrogenised
electrode, and the stronger acid might be expected to do this the more
readily. And it follows that with a given strength of acid, the amount
of free gaseous hydrogen should bear some relation to the rate at
which the electrolysis takes place : for were the gas freed from its
nitric radicle more slowly, or not faster than it could pass into the
occluded condition, none should bubble through the liquid ; but were
the rate of production of the element greater than that at which it is
absorbed by the platinum electrode, some should escape, the quantity
depending on the excess of the former over the latter action. This
view offers a satisfactory explanation of the general results so far as
they go, obtained by both Faraday and Bourgoin, and our own ex-
periments on the electrolysis of the acid still further increase its
probability.

The apparatus used by us was Hofmann's arrangement for illus-
trating the composition of water electrolytically. Each experiment
went on until the same quantity (35 c.c.) of oxygen collected at the
anode. The results, with other particulars, are given in the annexed
table (p. 3).

It may be observed that no free hydrogen was liberated in any of
the experiments with the 68 per cent. acid, nor in the first with the
1 : 1 acid; but in the second experiment with this strength, where the
rate of decomposition was five times greater than in the first, some
was set free; in the third, where the decomposition proceeded still
more rapidly, more ; and in the fourth, where again it was faster, still
more gas escaped oxidation. The same general result is obtained with
the weakest acid, but the proportion of free hydrogen for a given
battery power is much greater. Our explanation is, that in all the
experiments of the first series, as in the first of the second, the hydro-

Grove's cells employed.	Strength of nitric acid.	Time of experiment.	Negative pole.		
			Reduction in c.c. of oxygen.*	Free hydrogen.	H equal to NH_3 found.
1 ⎰	1 / 68·2 p.c. ⎱	3 hours	31 ·5	Nil	Nil
2	,,	55 mins.	28 ·4	,,	,,
4	,,	22 ,,	28 ·8	,,	,,
8	,,	10 ,,	29 ·4	,,	,,
1	1 : 1	3 hrs. 35 mins.	30 ·6	Nil	Nil
2	,,	42 mins.	29	2 c.c.	,,
4	,,	19 ,,	24 ·2	9 ,,	,,
8	,,	8 ,,	16 ·8	22 ,,	Trace
2	1 : 2	61 mins.	17	30 c.c.	2 c.c.
4	,,	18 ,,	0 ·5	65 ·7	Nil
8	,,	8 ,,	0 ·3	68 ·7	,,

gen was occluded at least as fast as produced—in fact, it is probable that at no moment in any of these trials was the platinum electrode fully charged with hydrogen: but that in the second experiment of the second series the gas was produced a little more rapidly than it was absorbed and oxidised; in the third experiment more, and in the fourth still more; whilst in the third series the same relation obtains, but the weaker acid being less readily deoxidated by occluded hydrogen, a greater quantity of the gas escaped through the liquid than in the corresponding trials with the stronger acid.

There is one very curious feature of this action to which we would now direct attention. In the second, third, and fourth experiments with the 1 : 1 acid, the evolution of hydrogen gas at the cathode ceased almost entirely and quite suddenly in three minutes, and in the first experiment with the 1 : 2 acid in 40 minutes. This evolution of hydrogen at the beginning only of the electrolysis of nitric acid was noticed by Bourgoin, and some long time previously by Schönbein. The first of these investigators made no attempt to account for the fact, while the latter attributed it to some *peculiar* condition into which the platinum electrode becomes thrown. We, on the contrary, have traced it to the presence of nitrous acid, which we find almost entirely prevents the escape of hydrogen with a battery power of 8 cells, when present in the proportion of 0·059 gram to 100 c.c. of the 1 : 1 acid.

The study of the action of the copper-zinc couple on aqueous nitre

* Determined by permanganate of potassium.

solution taught us that nitrite and nitrate of potassium suffer, when in admixture, simultaneous decomposition, and it would appear that the same obtains with their hydrogen analogues; and, moreover, that the mixture oxidises hydrogen more readily than does nitric acid alone.

Occluded Hydrogen and Nitric Acid.

Nothing is known, so far as we are aware, regarding the action of occluded hydrogen on nitric acid, but Dr. Armstrong (*Chem. Soc. J.*, 1877, **2**, 82) found hydrogen in the gaseous products of the action of nitric acid on a sample of nickel which Dr. Russell had prepared by reducing its oxide in a current of the gas, and inferred that it was hydrogen which had been occluded, and therefore escaped oxidation. He suggested this also as a means of investigating hydrogen-palladium.

The metal platinum, as is well known, is not attacked by nitric acid, and readily occludes hydrogen. For these reasons the gas was associated with this metal in order to study its action on nitric acid. A quantity of the metal was obtained in the most favourable form by precipitation with an alkaline formate. To ensure freedom from possible reducing matter, after being thoroughly washed and dried, it was boiled with strong nitric acid, again washed, and once more dried with as little contact with the air as possible. Nitric acid was not in the least acted upon by the metal thus prepared. The pure finely divided platinum was then charged with hydrogen by heating to 100° C. and cooling in that gas.

In a preliminary experiment, it was found that on dropping some pure nitric acid (68 per cent.) on to about 30 grams of the elements, a violent action was at once set up, the heat produced being sufficient to render the metal red hot, and to make us greatly fear an explosion, which convinced us that occluded hydrogen has, in this combination at least, a very decided action on nitric acid. A quantitative experiment was made by pouring very quickly 40 c.c. of the same colourless acid on 20 grams of the hydrogenised metal, when signs of reduction were almost at once noticeable by the yellow colour of the liquid and the escape of a small quantity of nitrous fumes. In 15 minutes the liquid reduced a quantity of potassium permanganate corresponding with 0·0372 of nitrous acid, and contained 0·0025 gram of ammonia. In another similar trial but with 1 : 1 acid, the reduction in 15 minutes corresponded with only 0·015 gram of nitrous acid, and 0·0016 gram of ammonia, showing still further the analogy between the action of electrolytic and occluded hydrogen on nitric acid.

But although the fact is thus satisfactorily established that hydrogen, when associated with a metal not acted upon by nitric acid, may be readily oxidised by it, such might not be the case were the gas

associated with a metal that is itself acted upon by the acid. Now, palladium both occludes hydrogen and is acted upon by nitric acid, especially when the latter contains nitrous acid, and therefore we thought an experiment with palladium-hydrogen and nitric acid might give results of some interest in settling this point. 2·5 grams of palladium were associated with about 120 c.c. of hydrogen, and some 18 c.c. of 1 : 1 acid quickly poured on. The metal slowly but completely dissolved without a trace of gas being set free, from which it would appear that whether the hydrogen be associated with a metal itself acted upon or not, it is still readily oxidised by nitric acid.

### Nascent Hydrogen and Sulphuric Acid.

Again, the only source of nascent hydrogen available is that from the electrolysis of the acid. Faraday, who investigated this action also in 1834, found that oxygen separated at the anode, and sulphur and pure hydrogen at the cathode (*Phil. Trans.*, 1834).

On studying this subject in the Hofmann's apparatus mentioned above, with pure redistilled oil of vitriol containing 98·2 per cent. H_2SO_4, and variable battery power, results were obtained agreeing with Faraday's. We observed, moreover, that immediately the action was started with two or more cells, the sulphur formed a film over the negative electrode, which increased but only with comparative slowness during the continuance of the experiment. This is significant, and no doubt has a very considerable influence on the relative proportions of the two elements set free, and very probably accounts for the appearance of free hydrogen at all, at least where the smaller battery power was employed : for this film must necessarily retard the occlusion of the freed hydrogen, and, therefore, according to our view, compel the greater part of the gas to escape out of the liquid. Evidence of the correctness of this reasoning was given by very carefully noting the amounts of gas set free in the first minute or two of the action, starting first with a clean and afterwards a sulphur-covered plate. With the latter a greater quantity of hydrogen always escaped for an equal amount of gas collected at the anode.

An idea of the amount of gas which escapes with different battery power, may be gathered by glancing at the annexed table. In each case the electrolysis went on until 11·5 c.c. of gas (oxygen, but with some ozone) had collected at the anode :—

Battery power.	Time.	Hydrogen.
2	3 ·5 hours	18 c.c.
4	1 hour	23 ,,
8	23 mins.	26 ,,

It might be expected that hydrogen acting on sulphuric acid would set free sulphurous anhydride thus :—

$$H_2SO_4 + H_2 = 2H_2O + SO_2.$$
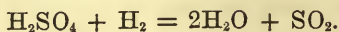
We could not, however, detect this substance in any of the experiments just detailed. But the reason of this, we thought, might be found in the quantity of the occluded gas being at any moment of the experiments sufficient to combine, apparently in one operation, with the three available atoms of oxygen in the acid molecule; and that if the gas were presented much more slowly, evidence of this very natural chemical change would be forthcoming. An experiment was therefore started with one cell. The amount of action was exceedingly small, only about one and a half c.c. of gas being collected at the anode in ten days. At the cathode not a trace of gas or sulphur appeared, but the liquid there was found to contain an appreciable amount of sulphurous anhydride.

It appears, then, that hydrogen, when associated with platinum, reduces oil of vitriol very readily, and that when the gaseous element is present in very small quantity, sulphurous anhydride is one of the products. The appearance of sulphur on the metallic electrode always results, very probably, from the complete deoxidation of this latter compound, which is much facilitated, no doubt, by the viscosity of the medium in which it is produced. Proof that occluded hydrogen does really bring about this reduction of sulphuric acid we now give.

Occluded Hydrogen and Sulphuric Acid.

Palladium Hydrogen.—The metal was obtained in a finely divided condition, and hydrogenised in the usual manner. On heating for one hour at 100° in a current of carbonic anhydride, as described below, 5 grams of the non-hydrogenised metal with 10 c.c. of the 98·2 per cent. acid, little or no sulphurous anhydride was evolved; but on pouring a few c.c. of the acid on a little of the metal charged with hydrogen, the odour of the sulphurous gas was immediately noticeable. The fact that sulphurous anhydride is abundantly evolved under these circumstances was completely established by quantitative trials, particulars of some of which we subjoin.

Experiment A. 10 c.c. of the acid were poured on 5 grams of the hydrogen-palladium. The sulphurous anhydride as produced was driven from the acid which absorbs it, by bubbling carbonic anhydride through the liquid. This was continued for 40 minutes at the ordinary temperature, and five minutes at about 100°. The amount of sulphurous gas which formed was found by iodine solution to be 0·592 gram.

Experiment B. Similar to A. The sulphurous anhydride was, however, estimated at intervals, when it was found that—

0·457 gram formed in the first 30 minutes, at the ordinary temperature.

0·152 gram formed in the next 30 minutes at 100°, and

0·001 gram formed in the next 30 minutes at 100°,

making a total in the hour and half of 0·61 gram.

Experiment C. Used 20 c.c. of the acid. In all other particulars the same as B. The amount of sulphurous anhydride formed was—

0·344 gram in the first 30 minutes, at the ordinary temperature,

0·261 gram in the next 30 minutes at 100°, and

0·016 gram in the next 30 minutes, at 100°,

making a total of 0·621 gram.

Oil of vitriol, then, not only very readily oxidises occluded hydrogen, but, it would appear, from the amounts of sulphurous anhydride produced in the several experiments being almost identical, that a definite proportion of the gas (some 72·4 per cent.) when associated with palladium, suffers this change.

Hydrogen-palladium has also a very slight reducing action on sulphuric acid mixed with an equal bulk of water.

Hydrogen Platinum.—Hydrogen associated with finely divided platinum prepared as already described, reduces oil of vitriol to sulphurous anhydride, but much less energetically than palladium-hydrogen.

Two views appear to be held with regard to the formation of the reduction-products in the action of metals on nitric acid and oil of vitriol : one that they result from the direct reducing action of the metallic elements ; the other, that the reductions are effected by nascent hydrogen produced by the initial action of the metals on the respective acids. These views are alike, in so far that both are based upon analogical rather than on experimental evidence. The first derives support from the fact that certain non-metallic elements are oxidated by the bodies in question; and the second, from the general behaviour of metals with the class of compounds designated acids.

Reasoning on the lines of this research, we saw that direct proof of the truth of the second, and more probable view, might not be impossible to find. Now, in order to obtain the evidence of the liberation of hydrogen which this view requires, it appeared only necessary to bring about the initial action at such a rate, that the liberation of the gas should be faster than it could pass to the occluded condition. And to ensure the greatest probability of doing this, it further appeared necessary to employ, firstly, the metal of maximum available activity, and, secondly, a large volume of acid relatively to the metal, in order to minimise the influence of reduction-products. Magnesium was natu-

rally suggested.   In each of our experiments a piece of this metal in thin sheet ($1 \times \frac{5}{8}$-inch), weighing 0·4 gram, was placed in the centre of 350 c.c. of the nitric acid liquid.

Experiment I. Used 68 per cent. acid.   The metal became coated at once with a whitish powder, and very slowly dissolved, with evolution of a minute quantity of gas, the liquid, as the action proceeded, acquiring a yellow colour.   In 54 minutes the metal remaining undissolved suddenly decomposed the acid, with almost explosive violence.   The total gas collected measured only 3 c.c.   It was neither combustible nor explosive.

Experiment II. Used 1 : 1 acid.   The metal did not tarnish, but entirely dissolved in 1—2 seconds, with evolution of gas, the first 3 c.c. of which burnt almost noiselessly; the second 3 c.c. detonated slightly ; and the next 6 c.c. burnt still more explosively.

Experiment III. Used 1 : 2 acid.   The general result was the same as in II.   A little more gas was evolved, and the first 3 c.c. burnt somewhat less noiselessly than the corresponding portion in II.   Further evidence of the production of hydrogen appeared unnecessary.

Among other results of this investigation, then, we may claim to have demonstrated the possibility of the replacement of hydrogen in nitric acid by a metal, a fact which very greatly supports, and removes from the region of conjecture, the view which regards the reduction-products already referred to, as formed by the direct action of hydrogen. We may also claim to have established still more fully the close likeness of character, and therefore of condition, between hydrogen usually denominated *nascent*, and hydrogen occluded by metals.

ON DRY COPPER-ZINC COUPLES AND ANALOGOUS AGENTS.

By J. H. GLADSTONE, F.R.S., Ph.D., and ALFRED TRIBE, Lecturer on Chemistry in Dulwich College.

In the Journal of the Chemical Society (1877, i, 567) we described in detail the mode of procedure for preparing what we have styled "dry couples," in contradistinction to ordinary copper-zinc couples, the latter from their very mode of formation being necessarily associated with water. Briefly, it consists in depositing the metal contained in a certain volume of a 2 per cent. solution of copper sulphate, on a given weight and surface of crumpled zinc foil, washing the conjoined metals with water to remove zinc sulphate, then with alcohol to remove the water, subsequently with ether, and finally heating the metals in a current of hydrogen to remove ether and any traces of water, and to bring about the disintegration of the foil. All this involves time and not inconsiderable trouble, and the necessity of employing expensive liquids as ether and alcohol is a decided disadvantage. Of course, when the object is to study the power of a new agent, or to employ it in the preparation of a valuable body, such considerations are of little moment; still anything which would lighten the labour or lessen the cost attending its use would be deserving of welcome.

Six years ago we pointed out the value of the dry couple in the preparation of zinc-ethyl, and since that time we have shown its applicability to the preparation of other zinc ethers. But our recent success in this direction in obtaining 99 per cent. of the theoretical yield of zinc methyl, which valuable reagent could only be satisfactorily obtained before by the substitution of zinc for mercury in the highly poisonous compound mercuric methide, led us to think of the possibility of simplifying the preparation of the dry couple. More especially did it seem desirable to dispense, if possible, with the use of the ether and alcohol.

It was obvious that these liquids could be dispensed with only by a

radical change in the method of bringing about the mechanical associa-
tion of the copper and zinc. Our first attempts towards doing this,
which consisted in mixing zinc filings with variable amounts of finely
divided copper, and subjecting the mixture to pressure in a steel tube,
were attended with but very imperfect success. The cause of the
practical failure of this method was, however, soon discovered. It was
noticed when the cylinders of the compressed metals were struck per-
pendicularly to their axes, which it was necessary to do in order to
reduce them to small pieces, that the contact of the dissimilar metals
had been only partially effected. It now occurred to us that this
mechanical association which is so absolutely necessary might become
more perfect were the metals after compression heated to the point
where zinc begins to change its physical condition, and it was thought
that in order to prevent oxidation, this heating might advantageously
be done in hydrogen gas. The success of the experiments which
resulted from the first anticipation was beyond our most sanguine ex-
pectations.

The activity of the new couple was ascertained by observing the rate
at which 5 c.c. of ethyl iodide was converted into zinc ethiodide. The
flasks containing the materials, to which inverted condensers were
attached, were heated by immersion in water at 90° C. In each trial
9 grams of zinc filings were used. The amounts of copper, which
varied for each experiment, with other particulars, are set out in the
annexed table :—

Compressed Metals in Hydrogen.

Expt.	Copper.	Time for conversion into ethiodide.
I	4·0 grams.	60 minutes.
II	2·0 ,,	13 ,,
III	1·0 ,,	8 ,,
IV	1·0 ,,	9 ,,
V	0·5 ,,	8 ,,
VI	0·25 ,,	14 ,,
VII	0·125 ,,	29 ,,

It results from these experiments that the relative weights of copper
in the same physical condition exert a very considerable influence,
and that a dry couple, almost equal in activity to the original dry
couple, can be prepared in any quantity without the aid of ether or
alcohol.

The activity of the several couples bears, no doubt, some close rela-
tion to the number of *separate* contacts between the dissimilar metals
in each case.

We now experimented with the object of ascertaining the value of the compression. The results obtained without compression given below show that it is of but little importance :—

Non-compressed Metals in Hydrogen.

Expt.	Copper.	Time for conversion into ethiodide.
VIII ..	1·0 gram.	9 minutes.
IX ..	1·0 ,,	10 ,,
X ..	0·5 ,,	12 ,,
XI ..	0·25 ,,	19 ,,

In the hope of still further simplifying the preparation, we experimented with couples prepared without compression, dispensing also with the heating in hydrogen. When the heating was effected in a flask open to the air, the activity of the couples produced was found to be much smaller; but when it was done in a flask provided with a cork through which passed a tube with a capillary opening, which was closed by fusion as soon as the heating was discontinued, the activity of the resulting couples to our astonishment was found to be actually greater than the activity of those prepared in hydrogen. The results of four experiments made in this way at different times are tabulated below :—

Non-compressed Metals in Air.

Expt.	Copper.	Time for conversion into ethiodide.
XII....	1·0 gram.	6·0 minutes.
XIII....	1·0 ,,	7·5 ,,
XIV....	1·0 ,,	7·0 ,,
XV....	1·0 ,,	6·0 ,,

The time required to bring about the conversion of the ethyl iodide by the old dry couple containing very nearly 9 grams of zinc is from six to nine minutes. Our success was therefore complete. Why a small quantity of air should be actually advantageous will be discussed presently.

We now describe in detail the method for preparing the most effective couple.

Place in a dry flask coarse zinc filings and finely divided copper in the proportion of 9 grams of the former to one of the latter, and fit to its mouth a cork bearing a glass tube through it with a capillary ter-

mination. After mixing the metals by shaking, immerse the bulb of
the flask, held horizontally, in a moderately hot Bunsen flame. The
flask is now so twisted by a jerking motion of the wrist, that the
metals are continually thrown over, until the filings just begin to lose
their shape and acquire a yellowish tinge, then shake somewhat
rapidly first in the flame and afterwards away from it. The heating
of the metals in the quantities hitherto employed usually takes from
one to two minutes. When the manipulation has been successful, a
number of dark grey small granular masses without metallic lustre
are obtained. When the heating has not been sufficient the shape of
the filings is more or less discernible, and when the heating has been
excessive the metals resemble semi-fluid yellowish shot, slightly
lustrous in appearance. This latter condition, in which in all proba-
bility the metals are chemically associated in an alloy, is absolutely
fatal.   The phenomena, however, which accompany its production
being so marked, enable the operator, after a very little experience, to
distinguish it readily from the true " couple condition."

Condition of the Metals employed.

Zinc.—The zinc used in these experiments was in coarse filings,
made from ordinary commercial sheet zinc by a zinc worker's coarse
single cut file.

Copper.—The copper first used was precipitated by zinc from a
moderately strong solution of its sulphate, then thoroughly washed
with water, dried and heated in a current of hydrogen. It was in a
fairly fine state of division, and light chocolate in colour.

As might be expected, the state of division of the copper is of great
importance. Experiments made to obtain definite knowledge on this
point showed that when the metal was in comparatively coarse parti-
cles, as in very fine filings, the activity of the couple of which it formed
part was very much smaller; and when the copper was in as fine a
condition as it is possible to obtain it by precipitation from a weak
solution of its sulphate, the difficulty of preventing the two metals on
heating from passing from the couple to the inactive condition was
much augmented, so much so in fact, as to render the operation one
requiring extreme care. These facts, conjoined with a knowledge of
the labour involved in the preparation of suitable copper by different
methods, induce us to recommend that condition of the metal which
may be obtained by the reduction of its protoxide at the lowest pos-
sible temperature in a current of hydrogen, and sifting the product
through fine muslin. Specimens prepared in this way from the
powdered black oxide used in combustion analysis, gave couples equal
and slightly exceeding in activity the most active ones employed in
this inquiry.

Experiment on a Larger Scale.

For the solution of the problem set before us, it has been sufficient to work on a comparatively small scale, but there appears nothing in the nature of any of the operations described to prevent them from being successfully performed on a much larger scale. To remove all doubts on this point, we determined to make an experiment on the preparation of zinc ethyl by our new couple, employing 87 grams of ethyl iodide and a proportionate quantity of couple.

The 90 grams of zinc filings used and the 10 grams of copper (from the oxide) were heated in the manner already described by a somewhat large Bunsen burner, in a 300 c.c. flask. This occupied five minutes. The mechanical association of the metals was not so perfectly effected as it is possible to associate them by heat, which arose from excess of caution. A little experience would be alone required to bring about the complete success of the operation, on whatever scale attempted. The 87 grams of ethyl iodide were now poured into the flask (to which an inverted condenser was attached) containing the couple, and the whole was heated by immersing the lower part of the bulb of the vessel in water at about 90° C. The liquid boiled in a few seconds, in nine minutes a large number of small bubbles appeared, a sure indication of rapid action, and in 15 minutes the conversion into ethiodide was complete. This completion is easily recognised by no more liquid iodide dropping again into the flask from the condenser. The flask was next attached to an ordinary condenser filled with dry hydrogen, and heated in an oil-bath, when at about 160° C., distillation began, which continued for 30 minutes. The zinc ethyl obtained was free from iodide, and weighed 31 grams. The 87 grams of ethyl iodide could produce theoretically 34·3 grams. We have, therefore, obtained 90·4 per cent. of the theoretical amount.

Couples of various Elements.

We have not hesitated in our papers to call the agent which we employ "the copper-zinc couple;" although aware that this has frequently led to misapprehension. The term suggests to many minds the metallic elements of a voltaic battery, and the first impression conveyed has frequently been that we were using a battery of low intensity with its conducting wires, &c. We have, however, purposely retained the term, because we have all along believed that the action was really of the same character as that which takes place in ordinary electrolysis, and indeed was identical with what occurs within the voltaic cell. There are the two metals in contact, standing in the decomposable liquid, only instead of one pair of plates, or several pairs joined together, we have minute pieces of metal, forming myriads of

circuits. There is this great advantage also in our arrangement, that the resistance of the binary compound is reduced to a minimum, as it washes the very points of contact of the metals.

Of course it follows from this view that if we were to employ metals wider apart than copper and zinc in the strength of their chemical affinities, or in other words which give a greater difference of potential, we might expect a more energetic action. Perhaps, too, we should be able to split up compounds which are capable of resisting the couple we have usually employed. Indeed, in our first paper on the subject, we showed that this increased action did not occur: for on employing platinum instead of copper with the zinc, we obtained a much more rapid decomposition of water. From experiments subsequently made and partially communicated to the British Association, it would appear that the power of the copper-zinc couple to decompose water is almost *nil* at 0° C., and very great near the boiling point of the liquid. In fact $1\frac{1}{2}$ metres of zinc foil 5·5 cm. wide, on which copper had been deposited, was placed in pure ice-cold water, and heated by various stages, the amount of hydrogen produced at each stage being ascertained. The results are given in the table below. We have repeated the experiment with the same amount of zinc foil on which platinum was deposited, and obtained the following comparative figures:—

Temp.	Copper-zinc.		Platinum-zinc.	
	Time.	Hydrogen.	Time.	Hydrogen.
2° C. ..	3 hrs.	3·3 c.c.	5 mins.	1·65 c.c.
22 ,, ..	2 ,,	11·1 ,,	,,	7·3 ,
34 ,, ..	45 mins.	10·4 ,,	,,	8·25 ,,
55 ,, ..	15 ,,	15·5 ,,	,,	28·0 ,,
74 ,, ..	10 ,,	29·1 ,,	,,	105·0 ,,
93 ,, ..	5 ,,	44·0 ,,	,,	150·0 ,,

These figures calculated for one hour at each temperature, give the following comparison:—

Temp.	Hydrogen per hour.	
	Copper·zinc.	Platinum-zinc.
2° C. ..	1·1 c.c.	19·8 c.c.
22 ,, ..	5·5 ,,	87·6 ,,
34 ,, ..	14·0 ,,	99·0 ,,
55 ,, ..	62·0 ,,	336·0 ,,
74 ,, ..	174·0 ,,	1260 0 ,,
93 ,, ..	528·0 ,,	1800·0 ,,

The results obtained with the copper-zinc couple give a curve represented in the following diagram:—
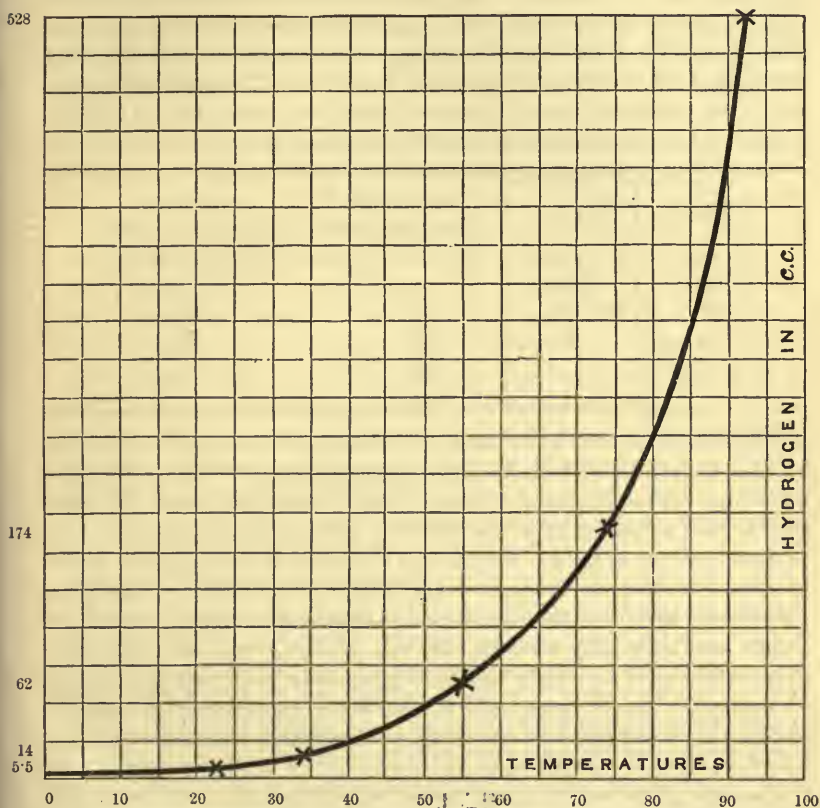
This shows clearly that the action is very small, even at the ordinary temperature, but that it becomes very rapid indeed near the boiling point. It would have appeared still more rapid if the action of the couple had not been considerably reduced by this time, through the formation of zinc oxide. This latter action produces a still more serious irregularity in the results with the platinum couple. But it is evident that the more negative metal platinum is capable of inducing considerable effect on water at a temperature at which copper is almost without influence, namely near the freezing point. It is probable also from the experiment, that the superiority of platinum is not maintained in the same proportion at temperatures where both the couples are very effective.

In the experiments just described the quantity of the negative metal

was not determined, but we know from previous work, that the superiority of the platinum is maintained even when its weight is actually less than that of the copper in the comparative experiment, and also that the result is the same with a different positive metal. Thus in some experiments with aluminium couples, communicated to the *Phil. Mag.*, in 1875, in which ·43 gram of copper and ·2246 gram platinum were each deposited upon 6 grams of aluminium foil (126 cm. by 5 cm. wide), results were obtained as in the following table :—

Temp.	Time.	Al-Cu expt. Hydrogen evolved.	Al-Pt expt. Hydrogen evolved.
12° C. ..	22 hrs.	2 ·5 c.c.	4
100 ..	next 6 ,,	375 ,,	484
,, ..	,,	92 ,,	114
,, ..	,,	55 ,,	78
,, ..	,,	33 ,,	45

The formation of a good couple depends, however, on other circumstances than the electromotive force of its elements. One very essential thing is that the negative metal should stick well upon the zinc, and in this respect copper was found to have a great advantage over platinum, silver, or gold. Further, in the making of couples by means of solutions of salts, the more active couple acts itself so rapidly on the water, that the zinc becomes considerably oxidised before the metals are thoroughly washed. It was evident, however, that these objections would not apply to the couples made in the dry way, and it was certainly worth investigation whether a more powerful combination could not be prepared than zinc and copper. The following combinations have been tried :—

Zinc and Silver.—The silver was obtained in a fine crystalline powder by precipitation from the nitrate by means of copper. It was mixed with zinc filings in the manner already described. 9 grams of zinc and 5 c.c. of ethyl iodide were used, with varying proportions of silver. Action took place, and was measured as before.

Expt.	Silver.	Time for conversion into ethiodide.
XVI ..	0·5 gram.	9 minutes.
XVII ..	1·0 ,,	5 ,,
XVIII ..	1·0 ,,	6 ,,
XIX ..	2·0 ,,	13 ,,
XX ..	3·0 ,,	15 ,,

It appears, therefore, that a dry couple, consisting of 1 gram of silver

to 9 grams of zinc equals if it does not exceed in strength the best dry copper-zinc couples.

Zinc and Platinum.—The platinum was prepared in fine powder by precipitation with an alkaline formate. It was heated with zinc filings, but before the zinc fairly softened, the two metals combined together with deflagration. Three experiments, however, were made with couples so prepared:—

Expt.	Platinum.	Time for conversion into ethiodide.
XXI ..	1 gram.	18 minutes.
XXII ..	2 ,,	30 ,,
XXIII ..	3 ,,	38 ,,

This poor result was in all probability due to the fact that the two metals alloyed. We therefore shook up some zinc filings with the platinum, and tried the mixture upon ethyl iodide. It did not act at all at the ordinary temperature during 24 hours, but neither did a similar mixture of finely divided copper and zinc filings. At the boiling point, the mixture of zinc and platinum gave 0·8 per cent. of the total action.

Zinc and Palladium.—Palladium was obtained in a similar manner to the platinum above mentioned, and when heated with zinc filings, deflagrated in the same way. The proportion employed was 1 to 9, and the time required for transforming 5 c.c. of ethyl iodide was 20 minutes (Experiment XXIV).

Zinc and Gold.—Gold was also prepared in the same way. It did not deflagrate with zinc, but from the appearance of the mass under the microscope, it was concluded that the two metals had alloyed. The following times were obtained:—

Expt.	Gold.	Time for conversion into ethiodide.
XXV ..	1 gram.	13 minutes.
XXVI ..	2 ,,	10 ,,

Zinc and Carbon.—Cocoa-nut charcoal in powder was employed, but when heated with zinc, the two were found not to stick together; in fact the metal, being much heavier, separates from the mixture. Its action on ethyl iodide was very doubtful.

Zinc and Brass.—It has already been stated that when the zinc filings and copper are heated too strongly together, they combine and

form a couple, which is practically worthless. Under these circumstances the microscope reveals the presence of pieces of yellow brass. Now brass in fine filings was found to have no action whatever on ethyl iodide, even when the experiment was continued for five hours. In the light of the above facts, it seemed possible that brass, if associated with zinc, might render the latter active. On trying the experiment with brass filings mixed with zinc filings, in the proportion of 1 to 9, the conversion of the ethyl iodide took place in 27 minutes (Experiment XXVII). This is a good result when the imperfection of the union of the two metals is considered, in fact copper in similar fine filings mixed with zinc took a longer time to effect the change, which shows that brass must be about as good for the purpose as copper.

Magnesium and Platinum.—As magnesium is reputed to be a more positive metal than zinc, it might be expected to give a more powerful couple with copper or platinum. And so it does, for, as pointed out by one of us (*Proc. Royal Inst.*, 1876), if strips of magnesium foil be coated with finely divided platinum by immersing them in platinic chloride, and the resulting salts be washed away, a couple may be obtained which produces a most vigorous evolution of hydrogen when it is placed even in cold water. On attempting, however, to make dry couples with magnesium, serious difficulties were encountered. The metal is pretty sure to be protected by a coating of oxide, more or less thick, and magnesium does not possess that very convenient property of softening at a moderate heat, and allowing the other metal to sink into its surface, and thus form a perfect connection. Our experiments with dry magnesium, copper, platinum, or carbon-magnesium couples, gave no promising results.

Attention has already been drawn to the circumstance that a dry copper-zinc couple seems to be more powerful when it is prepared in the presence of a small quantity of air. It is known that the copper plates of an old-fashioned voltaic battery are the better for being somewhat oxidated, and Sir W. Thomson finds that the difference of potential between copper and zinc is actually increased by partial oxidation of the former. This led us to try couples in which the suboxide or even the protoxide of copper were the negative elements.

Zinc and Cuprous Oxide.—The dry couples were prepared in the manner described above, but with cuprous oxide obtained by precipitation from copper sulphate by means of glucose. The following were the results :—

Expt.	Cuprous oxide.	Time for conversion into ethiodide.
XXVIII..	0·5 gram.	7·5 minutes.
XXIX..	1·0 ,,	6·0 ,,
XXX..	1·0 ,,	5·0 ,,

Zinc and Cupric Oxide.—Similar experiments were made with the ordinary powdered black oxide of copper. The dry couple when properly made is dark grey, and almost black in colour. A puce colour indicates insufficient heating. The microscope shows a great number of minute metallic particles of the colour of metallic copper or brass. The following were the results obtained :—

Expt.	Cupric oxide.	Time for conversion into ethiodide.
XXXI..	0·5 gram.	7 minutes.
XXXII..	1·0 ,,	8 ,,
XXXIII..	1·0 ,,	6 ,,

These experiments indicate no great difference between the couples made with metallic copper or either of its oxides, but in order to test this matter more fully we made duplicate series of experiments in an investigation we have since commenced. The result of these experiments was in favour of the metallic copper, as will be seen by the following tables of results. The couples were quite comparable, each quantity of 10 grams being taken from a large specimen. 5 c.c. of ethyl iodide were used in each experiment. The first table gives the comparison for three different temperatures :—

Expt.	Temperature.	Copper oxide.		Copper.	
		Time.	Result.	Time.	Result.
XXXIV..	34° C.	20 mins.	Trace	20 mins.	Slightly more than in CuO experiment
XXXV..	54	20 ,,	More	20 ,,	More
XXXVI..	74	9·5 ,,	Complete	9 ,,	Complete.

The following table gives the result for various times at the same temperature (54° C.).

Expt.	Time.	Copper oxide.	Copper.
XXXVII..	20 mins.	Trace.	Slightly more than in CuO experiment
XXXVIII..	40 ,,	Slightly more	Slightly more
XXXIX..	60 ,,	,, ,,	Just completing
XL..	80 ,,	,, ,,	Complete

The general conclusion from all these experiments on couples, in which the zinc or the copper is replaced by some other body, is, that for practical purposes, no combination has yet been found superior to the copper-zinc couple prepared in the way described above.

"The Aluminium-Iodine Reaction." By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S., Lecturer on Chemistry in Dulwich College. Received June 10, 1880.

About four years ago we pointed out a reaction of iodide of aluminium which, as far as we are aware, has no precise analogue in the science of chemistry, and which has led to the discovery of several volatile aluminium alcohols. It is well known that neither water, alcohol, nor ether is decomposed by metallic aluminium, and that each of these bodies will dissolve iodine without entering further into combination with it; but we found that by the joint action of these two elements, it was possible to split up the above-mentioned liquids. Water, though forming a definite hydrate with the iodide of aluminium, is decomposed by it in the presence of an excess of the metal, hydrogen being evolved and aluminic hydrate formed. This takes place at the ordinary temperature.

Alcohol in a similar manner is decomposed by the joint action of metallic aluminium and its iodide, with the ultimate production of hydrogen gas, aluminic ethylate, and varying amounts of aluminic iodoethylate proportional to the quantity of aluminic iodide employed. A small quantity of the iodide suffices to bring about the formation of a very large amount of the ethylate; in fact, the process would be a continuous one, were it not that the solid products gradually put a stop to the reaction.

Ether is not affected by aluminic iodide and aluminium, but when exposed to iodine and aluminium simultaneously it suffers a violent decomposition, iodide of ethyl and the aluminic iodoethylate being the ultimate products.

Amylic ether behaves in a similar manner, and the acetates of ethyl and amyl give analogous results; but the reaction is not an ordinary

double decomposition, for it does not take place when ready-formed iodide of aluminium is employed.

The several changes thus described are typical of our "aluminium-iodine reaction." The reaction is quite distinct from that which has lately given beautiful results in the hands of Friedel; and we have investigated its applicability both for the production of new compounds, and for distinguishing between different classes of organic bodies, as well as for throwing light on their comparative constitution.

Neither zinc nor iron, nor, as far as we know, any other metal can be substituted for aluminium in this reaction; but the chloride or bromide may be used instead of the iodide, though with less advantage.

Recent Results.

For decomposing an alcohol a small quantity of iodine is dissolved in it, the necessary excess of aluminium is added, and the mixture is heated. Evolution of hydrogen gas begins immediately, and proceeds somewhat rapidly until the whole of the metal has passed into combination. In this way the aluminium derivatives of the following alcohols have been prepared:—Ethylic, normal propylic, iso-butylic, amylic, benzylic, phenylic, cresylic, and thymolic. The first four of these aluminium derivatives may be distilled *in vacuo*, and they have thus been separated from the other solid products of the reaction, and obtained in a pure condition. The other aluminic alcohols cannot be distilled, at any rate not without very considerable decomposition. The following alcohols, however, behaved in a different way with the reagent:—

Methyl alcohol is not decomposed by aluminic iodide and aluminium, but in presence of free iodine it parts slowly with hydrogen, and the same happens when an aluminium-platinum couple is substituted for the metallic aluminium.

Iso-propyl alcohol.—This is not acted upon in the least by the reagents.

Cetyl alcohol.—On heating this compound with the reagent, hydrogen is slowly set free, until the temperature reaches about 200° C., when another chemical change is set up, resulting in the formation of cetyl iodide and aluminic hydrate.

Allylic alcohol.—The first action is identical in character with that which takes place with the alcohols of the $C_nH_{2n+1}OH$ series. Instead, however, of the whole of the liberated hydrogen escaping, about 30 per cent. of it acts upon the excess of alcohol, splitting it up into propylene and water.

Ethene alcohol.—The reagent does not liberate hydrogen from this substance, and has but a very slight action upon it.

Propenyl alcohol.—No hydrogen is evolved, but a double decomposition ensues at about 140° C., yielding allyl iodide, free iodine, and

aluminium hydrate; if aluminium be in excess, aluminic hydrate and allylic iodide are the sole products.

Aldehyde.—Hydrogen is not set free from this compound.

The general result, then, of these observations is that the reagent substitutes aluminium for the basic hydrogen of water, and of all the alcohols hitherto tried, whether of the methyl, allyl, benzyl, or phenyl series, with the remarkable exception of isopropyl alcohol. On the other hand, it does not substitute aluminium for hydrogen in the dihydric or trihydric alcohols, nor yet with aldehyde. The reaction with the ethers and glycerine is of a different character, as, in addition to an aluminium compound, the iodides of the positive radicals are formed.

General Properties of the Aluminium Alcohols.

The aluminium alcohols are solid at the ordinary temperature, and fuse generally into clear liquids. They possess, in a marked degree, the property of remaining fluid far below their melting points. Those of the methyl series distil unchanged at reduced pressures, affording the first organic compounds which contain both oxygen and a metal and are capable of distillation. They are soluble more or less in ether, alcohol, and benzol, but are decomposed by water with the formation of aluminium hydrate and the alcohols.

They were found to have the following specific gravities at 4° C. :—

Ethylate	1·147	Phenylate	1·25
Propylate	1·026	Cresylate	1·166
Butylate	0·982	Thymolate	1·04
Amylate	0·980		

Action of heat.—All these alcohols are decomposed at a temperature somewhere about their boiling points, and it became an interesting subject of inquiry whether they were resolved into alumina, and the alcohol and its olefine, or into alumina and the ether. Both these actions seem to take place. Thus aluminic ethylate appears to be decomposed by heat in both ways, but mainly according to the following scheme :—

$$(C_2H_5O)_6Al_2 = Al_2O_3 + 3C_2H_4 + 3C_2H_6O.$$
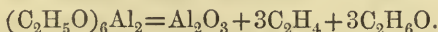
Aluminic phenylate on the other hand is capable of decomposition mainly in the following way :—

$$(C_6H_5O)_6Al_2 = Al_2O + 3(C_6H_5)_2O.$$
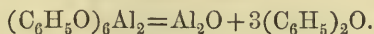
It must not however be supposed that these decompositions take place without other reactions. Some of the bodies thus produced are new ones, and we are at present engaged in their investigation.

The most interesting decomposition is that of the thymolate. When

heated it splits up into alumina, propylene, and bodies of the cresylic group. One of these is a solid body, which when resublimed or crystallised from alcohol presents itself in most beautiful pearly plates. Its properties resemble rather those of an ether, and concordant analyses of different specimens and determinations of vapour density give the anomalous molecular formula $C_{14}H_{13}O$, but its real constitution is still the subject of inquiry.

Theory of Reaction.

The reaction by which the compounds described above are formed is by no means clear at first sight. It is difficult to imagine that the presence of a haloid salt should determine the direct replacement of hydrogen by aluminium in water or in alcohol. We believe however that the presence of hydriodic acid in the reaction with the aromatic alcohols furnishes the true key to the chemical change. The first action is in all probability that of a reciprocal decomposition between two binary compounds—the alcohol and aluminium iodide—forming a certain proportion of aluminium alcohol and hydriodic acid. But the metallic aluminium present at the same time decomposes the hydracid with evolution of hydrogen and the production of more aluminium iodide, which brings about a further redistribution of the elements and the formation of more of the aluminium alcohol and the hydriodic acid, and so on till the chemical change is complete. The following equations express these changes, which take place alternately or rather continuously :—

(1) $6(C_nH_{2n-7}O.H) + Al_2I_6 = Al_2(C_nH_{2n-7}O)_6 + 6HI.$
(2) $6HI + Al_2 = Al_2I_6 + 6H.$
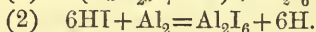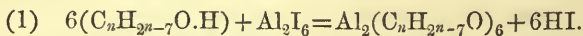
It is evident that as the iodine does not enter into the final products a very small quantity of it is sufficient to carry on the continuous chemical change.

There can be little doubt that the same reactions occur in the case of the alcohols of the $C_nH_{2n+1}O.H$ series, but the amount of hydriodic acid formed in the reciprocal decomposition is perhaps very small, and the tenacity with which it is held by the alcohol has made it impossible for us to prove its separate existence. The same remark applies also to water, which we believe to act in the same way. Indeed we know from the experiments of Roscoe that there would be no chance of separating minute quantities of acid from an aqueous solution under the circumstances.

The part which the free elements take in the decomposition of the ethers is doubtless analogous to that which the combined elements play in the action with water and alcohol. The reason why the free elements do, and aluminic iodide does not attack the ethers, is probably

owing to the available energy being greater in the former than in the latter case.

In conclusion, we would commend this aluminium-iodine reaction to the consideration of other chemists, who may be investigating organic compounds containing oxygen.
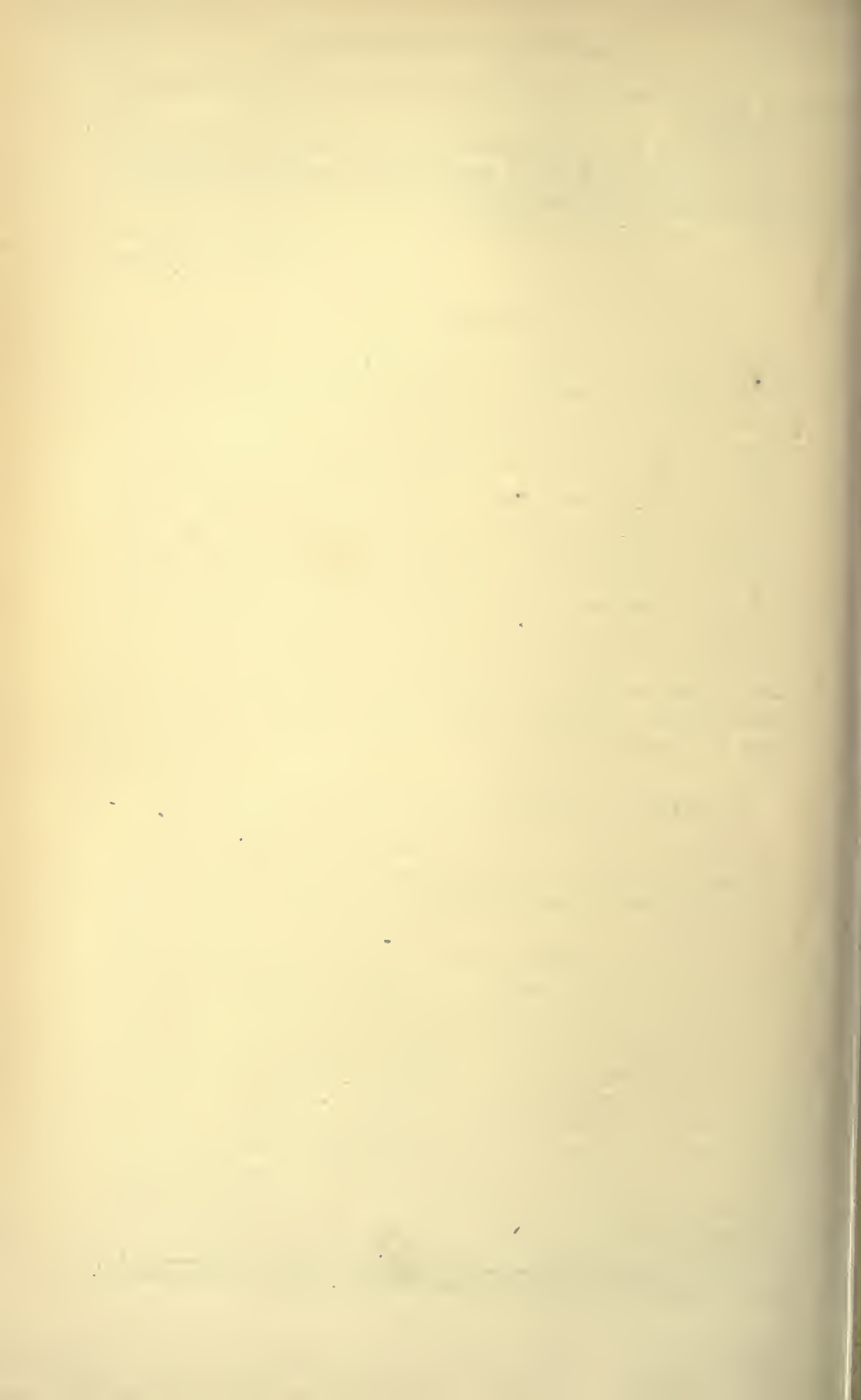
Note on Thermal Electrolysis.

By J. H. GLADSTONE, *F.R.S.*, and ALFRED TRIBE.

DURING the course of our experiments on metallic re-
placements we noticed that some sheet silver, immersed
in fused silver chloride, became quickly studded with crystals
of metal. A replacement of a metal by itself seemed so
anomalous, that our first idea was that the silver employed
contained certain impurities; but we found that the action
took place just as well with the purest silver we could ob-
tain, and that it was not restricted to the substances above
mentioned. Not only might the iodide of silver be substi-
tuted for the chloride with the same result, though not so
rapidly effected, but other metals might be employed. Thus,
when copper was immersed in fused cuprous chloride, crystals
of that metal separated ; and similar exchanges took place
when zinc was placed in melted zinc chloride, or iron in ferrous
chloride in a molten condition.

It was then thought that a different physical condition

* Read before the Physical Society on April 9.

of the rolled metals might give rise to the action; but this was disproved by the following experiments :—

Some crystals of silver prepared by electrolysis were placed in the open end of a piece of glass tubing slightly constricted, and then immersed in silver chloride heated in a crucible by a Bunsen lamp. In about half an hour the crystals were found to have grown in a net-like mass from their original position to a point about half an inch higher in the tube. This experiment was repeated with crystals of silver which had themselves been deposited from the fused chloride by means of metallic silver. A similar result was obtained.

We were then led to the conclusion that the change depended upon the unequal heating of different parts of the immersed metal, or rather of the salt in which it was immersed. It is evident that upon the contact theory of voltaic action, there will be a difference of potential between the metal and the liquid chloride with which it is in contact; and it is in accordance with analogy to suppose that this difference of potential will vary according to the temperature. Now, under the conditions of the experiment, it cannot be supposed that all parts of the fused chloride in contact with the immersed metal were always equally heated; and we have therefore the possibility of a current being established with the consequent electrolysis of the salt.

In order to test this view, some silver chloride was fused in a hard glass tube and a rod of silver placed in the liquid. On heating the underside of the lower end for 10 minutes, we found a considerable crop of silver crystals in the comparatively cool part of the fluid.

In another experiment some silver chloride was fused in a crucible, and one side of the vessel was more strongly heated than the other. Two long rods of silver were connected with a galvanometer and placed, one in the hotter, the other in the colder part of the chloride. The latter was found studded with crystals at the end of 15 minutes, whilst the former was quite clean. On repeating this experiment, it was always found that the galvanometer gave a larger deflection the greater the difference of temperature between the portions of the fused mass penetrated by the silver wires, and that the current was reversed with a reversal of the rods. Copper wires in cuprous chloride gave similar results.

In an experiment with an electrometer we obtained a clear indication of a difference of potential between silver rods in hotter and colder parts of silver chloride fused in a small crucible, the deflection showing a difference of possibly $\frac{1}{50}$ of a

volt. The reversal of the rods again produced a reversal of the deflection.

In corroboration of the theory above stated, it should be borne in mind that the chlorides of silver, copper, zinc, and iron, when fused, are electrolytes. The liquid chloride of tin is not an electrolyte ; and it was found that on immersing tin in this liquid no deposition of crystals was observed when it was so arranged that one part of the liquid was kept at the heat of boiling water and another at the ordinary temperature for two days ; nor was there the least action on a galvanometer when arrangements were made for testing by that instrument.

These experiments form a good lecture-table illustration of the conversion of heat into electricity and chemical force. They also seem to have a bearing on the theory of voltaic action, since, from the nature of the substances employed, it is difficult to imagine that chemical action in any way initiates the current.
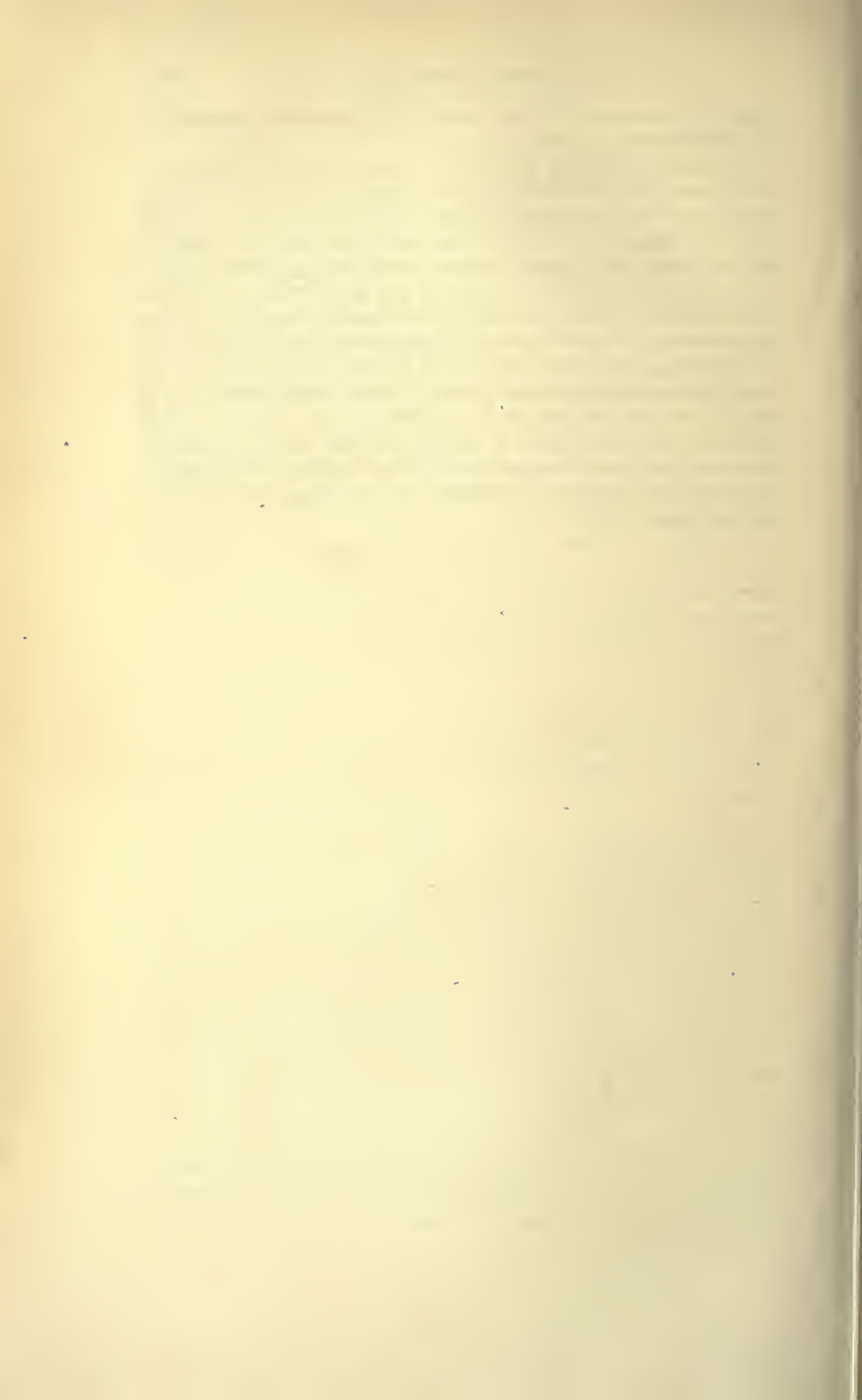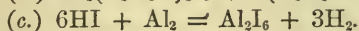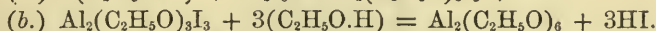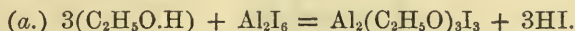
ALUMINIUM ALCOHOLS. Part I. THEIR PREPARATION BY MEANS OF THE ALUMINIUM-IODINE REACTION.

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.C.S., Lecturer on Chemistry in Dulwich College.

In a communication made to this Society in 1876, **29**, p. 158 of this Journal, we stated that aluminium or aluminium iodide singly is without action on absolute alcohol, but that together they decompose the liquid with facility. The resulting bodies are hydrogen and two new organic aluminic compounds, aluminic iodo-ethylate, $(C_2H_5O)_3I_3Al_2$, and aluminic ethylate, $Al_2(C_2H_5O)_6$. We showed too that the metallic iodide and the metal need not exist together in equivalent proportions, in order either to initiate or to continue this decomposition, and in fact that one molecule of the iodide suffices to bring about the combination of very many atoms of aluminium with the oxy-radical of the alcohol.* We also showed that the amount of hydrogen set free is equivalent to that of the metal which disappears, and is quite independent of the quantity of iodide present.

With regard to the part which this salt plays, two views were enunciated. The one for which we expressed a preference supposed that the reaction takes place through the intervention of intermediate bodies, thus :—

$(a.)\ 3(C_2H_5O.H) + Al_2I_6 = Al_2(C_2H_5O)_3I_3 + 3HI.$

$(b.)\ Al_2(C_2H_5O)_3I_3 + 3(C_2H_5O.H) = Al_2(C_2H_5O)_6 + 3HI.$

$(c.)\ 6HI + Al_2 = Al_2I_6 + 3H_2.$

* We have since obtained the combination of as much as 54 atoms of aluminium by means of one molecule of the iodide.

It will be understood that the complete conversion of the aluminic iodide into the iodo-ethylate, and this again into the ethylate, as by equations *a* and *b*, occurs only when the freed hydriodic acid is destroyed, as by equation *c*.

Whether, however, this be the true view, was not decided by our experiments. And it appears from both the suppositions referred to, that a relatively small quantity of the iodide should bring about the decomposition of an unlimited quantity of alcohol in presence of the metal. Such, it is evident, would be the case were it not for the mechanical interference of the solid products of the reaction.

In the present communication, we establish more completely our knowledge of the composition and properties of the ethylate, and describe the results obtained on applying the *aluminium-iodine reaction* (*Proc. Roy. Soc.*, 1880, 546) to the preparation of analogous aluminium derivatives of other alcohols.

General Instructions.

Into a flask, fitted with an inverted condenser, place the alcohol, aluminium, and iodine in the proportions of 20* c.c. of the liquid, 2 grams of the metal, and 1 gram of iodine, and heat the substances by immersing the bulb of the vessel in boiling water. The elements quickly combine and produce the necessary aluminic iodide, and the decomposition of the alcohol begins before the whole of the free iodine passes into combination; and proceeds moderately rapidly until the metal disappears and the evolution of hydrogen stops. The contents of the flask are now heated to about 300° in an oil-bath, and continued at this temperature until distillation practically ends. The distillate consists of the excess of alcohol used, mixed generally with some of its iodide, which latter compound results from the decomposition in presence of alcohol of the intermediate iodo-body, very probably in accordance with the equation:

$$Al_2(C_nH_{2n+1}O)_3I_3 = Al_2O_3 + 3C_nH_{2n+1}I.$$
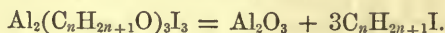
The flask is next attached to a receiver by means of a piece of short wide tubing, this receiver to another, and the second to a pump. The general arrangement is shown in the figure.

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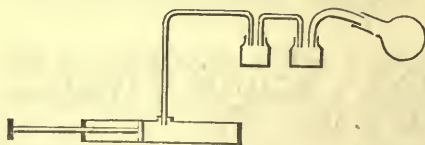
* With alcohols of high molecular weight, it is necessary to increase this volume to 30 or 40 c.c., and to heat to a higher temperature than 100° C.

The apparatus is now exhausted of air, the product in the flask melted and then heated till distillation is over, the pump being kept at work during the operation.   Some of the distillate usually passes into the second receiver, but the greater part always collects in the first.   Even when the vacuum is kept as perfect as possible some decomposition always occurs, the amount of which varies for the different compounds, as will be shown hereafter.   Of the alcohols already isolated in this way, the ethylate distils with the greatest, and the amylate with the least facility.

The aluminium used was in the form of foil, cut into small pieces, and of such a thickness that 1 gram measured 110 square centimetres.

Aluminic Methylate.

We have stated in the paper to which reference has already been made, that methyl alcohol is not affected when boiled with aluminium and aluminium iodide.   We find, however, that this liquid suffers some amount of decomposition when the iodide is formed in the boiling alcohol, but only while iodine remains in a free condition ; further, that when the metal is conjoined with platinum deposited from the chloride, the decomposition of the alcohol continues long after the whole of the iodine has passed into combination.

In an experiment employing 2 grams of aluminium coated with platinum, 2 grams of iodine, and 20 c.c. of methyl alcohol, 800 c.c. of hydrogen were set free in three hours, on heating to the boiling point of the liquid.   The atomic ratio of aluminium to iodine found in the residue was 1 to 0·62 ; and after 18 hours' heating, when the action was proceeding extremely slowly, 1 : 0·4.   These numbers, and the knowledge of what takes place under practically analogous circumstances with other alcohols of the same series, enable the composition to be assigned to the solid product of this reaction with a considerable degree of probability.   Calculating the iodine as iodo-compound, and the aluminium as methylate, and subtracting from this latter the methylate corresponding to the iodo-compound, 100 parts of the solid products when the experiment was stopped, would appear to consist of 55·6 parts of aluminic methylate, and 44·4 parts of aluminic iodo-methylate.   Attempts made to separate these compounds were not successful, owing probably to the unstable character of the methylate.

Aluminic Ethylate.

We supplement the directions which have already been published for the preparation of this compound, by giving the details of an experiment, following the plan described under the heading "general instructions."

2 grams of iodine, 4 grams of aluminium, and 40 c.c. of alcohol were heated as directed. The first litre of hydrogen collected in 5 minutes, the second in 4, the third in 10, the fourth in 16 minutes. Evolution of gas continued for 10 more minutes. The total hydrogen collected measured 4,345 c.c. (corrected). The product in the flask was solid, and on heating at 300°, and then *in vacuo*, gave 12·5 grams of distillate quite free from iodide.

Several quantities of the substance collected as described were found on analysis to contain from 1—2 per cent. of aluminium in excess of that which ethylate would require. This discrepancy we thought might very probably arise from decomposition of the distillate while in the receivers. The first estimation of aluminium was made in a part of the last portion of distillate collected in the upper part of the tubule of an ordinary condenser, the analytical details of which we now subjoin, and also the results of the analysis of two other specimens, which were collected in small quantities in cooled receivers, the object of this being to induce rapid solidification, and to minimise the influence of the diminished pressure.

 I. 1·062 gram dissolved in dilute nitric acid, and aluminium precipitated by ammonia and ignited, gave 0·330 gram Al_2O_3.

 II. 0·4465 gram of a different preparation, treated with water to decompose it, dried at 100° and ignited, gave 0·146 Al_2O_3.

 III. 0·272 gram burnt with oxygen and oxide of copper gave 0·4395 gram CO_2 and 0·2385 gram H_2O.

		Calculated.	Found. I.	II.	III.
Al_2	55	16·92	16·58	17·46	—
C_{12}	144	44·30	—	—	44·06
H_{30}	30	9·23	—	—	9·74
O_6	96	29·55	—	—	—
$Al_2(C_2H_5O)_6$ ..	325	100·00			

Considering the difficulties attending the purification, these analytical numbers accord sufficiently well with those calculable on the supposition that the body examined has an atomic composition agreeing with the formula $Al(C_2H_5O)_3$, and from analogy the molecular formula $Al_2(C_2H_5O)_6$. Such a compound receives the name of aluminic ethylate, it being evidently an analogue of Williamson's potassium and sodium ethylates.

Aluminic Propylate.

Normal propyl alcohol boils, according to Chancel, at 96—97°; to Rossi, at 96°; and to Pierre and Puchot, at 98·5°. The alcohol used for the experiments about to be described boiled at 96°.

2 grams of aluminium, 1 gram of iodine, and 20 c.c. of the alcohol were heated to 100°. The first litre of gas collected in 18 minutes, and the second litre in 33 minutes. The action slowly continued for 15 more minutes. The total hydrogen evolved measured 2,145 c.c. (corr.). On heating the residue to 300°, considerable frothing was noticed, and a non-fusible substance was left in the flask. This was found to be free from iodine, and gave on treatment with water and ignition 61 per cent. of alumina. From this it would appear to consist in 100 parts, of 52·1 parts of aluminic propylate and 47·9 of alumina, showing that some 78 per cent. of the organic aluminium compound had suffered decomposition. In another experiment a similar residue was gradually heated to 145°, when the frothing became decided, and it was then analysed. 0·423 gram gave on solution in nitric acid and addition of silver nitrate 0·006 gram of silver iodide; and 0·576 gram gave on treatment with water and ignition 0·156 gram of alumina. These data, and considerations previously referred to, lead us to assign to the residue at this stage the percentage composition of—

> 1·23 aluminic iodo-propylate,
> 96·08 aluminic propylate,
> 2·69 alumina.

It was now heated *in vacuo*. A quantity of alcohol passed over, followed by 1·8 gram of a dense liquid, which solidified on cooling.

This small yield of what presumably was aluminic propylate led us to think that the large amount of decomposition which must have taken place was occasioned by the alcohol containing water. A portion of it was therefore digested with anhydrous potassic carbonate, then with caustic baryta, which treatment increased the boiling point about a degree. An experiment made with it similar to the last gave, however, but a slight increase in the quantity of the aluminium distillate, viz., 2 grams. But in another trial, where the whole distillation was done *in vacuo*, 4·6 grams of the aluminium compound passed into the first receiver, which shows that the decomposition is mainly due to temperature.

Aluminium was estimated in each of the distillates, with the following results, stated in 100 parts:—

I.	II.	III.	$Al_2(C_3H_7O)_6$.
12·73	14·25	13·0	13·44

which numbers agree as well as could be expected, considering the nature and mode of preparation of the substance analysed, with those calculable on the supposition that the compound obtained as described is the third member of the series of aluminic alcohols, viz., aluminic propylate, $Al_2(C_3H_7O)_6$.

Isopropyl Alcohol.

In our paper on the action of the couple upon the two propyl iodides (*Chem. Soc. J.*, 1873, **26**, 961), it was pointed out that the iso-iodide was the more readily decomposed; and, further, that zinc iso-propide, which we obtained in small quantity, splits up at a temperature of 132° into zinc and hydrocarbon gases, whilst the normal zinc compound distils without material change at 146°. We have just shown that the normal alcohol decomposes readily in presence of aluminium and its iodide, and the fact of the greater instability of the two derivatives of the iso-alcohol led us to expect that it would undergo decomposition still more rapidly in presence of aluminium and aluminic iodide. On heating the reagent, however, with a specimen of the alcohol that distilled between 82° and 85°, not a trace of decomposition was observable, which unexpected result induced doubts as to whether the substance employed was really isopropyl alcohol. To place this matter beyond dispute, a portion of the specimen was boiled with strong aqueous hydriodic acid, when an oily compound was produced, having the boiling point and specific gravity of isopropyl iodide. This iodide, when heated to 50° with the copper-zinc couple, underwent decomposition in a manner which left no doubt regarding its being the iodide of isopropyl alcohol.

Aluminic Isobutylate.

Isobutyl alcohol boils, according to Linnemann, at 108·4°, and according to Chapman and Smith at 109°. The alcohol we have employed boiled at 108—109°. In an experiment where 4 grams of aluminium, 2 grams of iodine, and 40 c.c. of the alcohol were heated to 100°, the first litre of hydrogen was evolved in 7 minutes, the second litre in 4 minutes, the third in $3\frac{1}{2}$, and the fourth in $7\frac{1}{2}$ minutes. The action slowly continued for 15 minutes longer. The total gas collected measured 4,044 c.c. (corr.). The residue, after heating to 300°, was distilled *in vacuo*, when 16 grams of an aluminium compound free from iodide passed into the receivers. Portions of different specimens of this substance were analysed.

I. 0·478 gram dissolved in dilute nitric acid and aluminium precipitated by ammonia, gave 0·0982 Al_2O_3.

II. 0·689 gram, treated with water, dried at 100°, and ignited, gave 0·1473 Al_2O_3.

III. 0·2005 gram, treated as in II, gave 0·0425 Al_2O_3.

IV. 0·2457 gram, burnt with oxygen and oxide of copper, gave 0·5255 CO_2 and 0·226 H_2O.

These results, when set out as under—

		Calculated.	Found.			
			I.	II.	III.	IV.
Al$_2$..........	55	11·15	10·97	11·41	11·31	—
C$_{24}$..........	288	58·43	—	—	—	58·32
H$_{54}$..........	54	10·95	—	—	—	10·22
O$_6$	96	19·47	—	—	—	—
Al$_2$(C$_4$H$_9$O)$_6$..	493	100·00				

show that the body examined agrees in composition with the formula Al$_2$(C$_4$H$_9$O)$_6$, and, therefore, it being a derivative of the iso-alcohol, receives the name of aluminic isobutylate.

Aluminic Amylate.

The amylic alcohol of fermentation boils, according to various authorities, from 128—132°. That which we have employed boiled at 129—131°.

In illustration of the behaviour of aluminium and aluminic iodide with this alcohol, we subjoin the details of an experiment. 4 grams of the metal, 2 grams of iodine, and 40 c.c. of the alcohol were heated at 100°. The first litre of gas collected in four minutes, the second in two minutes, the third in two minutes, and the fourth in five minutes, showing that the action is decidedly more rapid with this than with the other alcohols. The total hydrogen obtained measured 3,985 c.c. (corr.). The residue heated to 300°, and *in vacuo*, gave 14 grams of an aluminium distillate, which, as well as another specimen prepared in like manner, were analysed.

I. 1·79 gram, dissolved, &c., gave 0·3056 Al$_2$O$_3$.

II. 0·6235 gram, treated with water, &c., gave 0·112 Al$_2$O$_3$.

III. 0·2815 gram, burnt with oxygen and copper oxide, gave 0·6455 CO$_2$ and 0·293 H$_2$O.

		Calculated.	Found.	
			1.	II.
Al$_2$............	55	9·53	9·12	9·59
C$_{30}$............	360	62·39	—	62·53
H$_{66}$............	66	11·44	—	11·56
O$_6$	96	16·64	—	—
Al$_2$(C$_5$H$_{11}$O)$_6$ ..	577	100·00		

The analytical numbers, as shown by the above statement of results, agree with the formula Al$_2$(C$_5$H$_{11}$O)$_6$, which is that of the fifth member of the series of aluminic alcohols, viz., aluminic amylate.

Cetyl Alcohol.

Methyl alcohol, as has been shown, does not undergo decomposition when boiled with aluminic iodide and aluminium, but this may arise from the low boiling point of the liquid. The difference in the rate at which the other alcohols part with hydrogen under analogous conditions is not well marked. The study of the action of the reagent upon a much higher member of the series it was thought would show definitely whether the stability of these compounds, which may be presumed to be of the same constitution, increases or not with their molecular weight, and also whether the replacement of hydrogen might be expected to take place in the intermediate members not examined.

Cetyl alcohol, $C_{16}H_{33}OH$, being the first solid member of the series, and sufficiently removed from amylic, was selected. This compound, gradually heated with Al_2I_6, underwent no visible change until between 200° and 250°, when action was indicated by the solidification of the melted contents of the flask. On treating this solid product with alcohol, aluminic hydrate was found in the residue, and cetyl alcohol and a solid organic iodide—presumably cetyl iodide—in solution. The action, therefore, appears to be one of double decomposition, and to accord with the equation—

$$6C_{16}H_{33}OH + Al_2I_6 = 6C_{16}H_{33}I + Al_2(HO)_6.$$
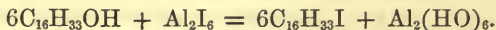
The alcohol gradually heated with Al_2I_6 and aluminium gave a little hydrogen; but at about 200° the gas evolution ceased, 100 c.c. having been collected. The contents of the flask were solid, and resembled the product of the action of heat on the alcohol and Al_2I_6 alone. On heating with free iodine and aluminium, about 150 c.c. of hydrogen were evolved as the temperature rose to 150°, when the evolution of gas quickly ceased as before, the contents of the flask having solidified.

In each of the experiments, 18·5 grams of the alcohol (about 10 c.c. when melted) were employed. In the first also 2 grams of Al_2I_6; in the second, 2 grams of Al_2I_6 and 0·5 gram of aluminium; and in the third, 2 grams of iodine and 0·5 gram of aluminium.

We conclude that cetyl alcohol is much more stable in presence of Al_2I_6 and aluminium than amylic alcohol, or the other members of the series which have yielded to these reagents, and that under their influence hydrogen is evolved and aluminic cetylate accordingly formed, but that the temperature at which this action takes place, being so close to that at which the double decomposition occurs previously referred to, prevents any quantity of this compound being produced.

Monohydric Alcohols of other Series.

Allyl alcohol.—After a preliminary trial or two, which showed that aluminic iodide could be boiled with this compound without either substance undergoing change, 2·2 grams of the iodide were dissolved in 20 c.c. of the alcohol, and heated with 1 gram of aluminium in the usual manner. Gas was slowly evolved for about an hour, when it almost ceased, 550 c.c. having been collected. The gas burned with a luminous smoky flame, and contained 37 per cent. by volume of an olefine, the remainder being hydrogen.

Another experiment was made by heating 20 c.c. of alcohol with 2 grams of iodine and 1 gram of aluminium. In 15 minutes 700 c.c. of gas were evolved, and in 10 more minutes action ceased. The whole of the aluminium was used up, and the gas collected measured 870 c.c., of which 270 c.c. were absorbed by bromine, the remainder being hydrogen. The compound produced by the union of a part of the gas with bromine, possessed the properties of propylene dibromide, showing that the hydrocarbon gas was propylene.

The explanation of these results is probably as follows:—The initial action is doubtless identical in character with that which takes place with the alcohols of the methyl series. In place, however, of the whole of the freed hydrogen escaping, as in the action with these compounds, about 30 per cent. of the gas, after decomposing the alcohol, enters into combination with both its negative and positive radicals, forming propylene and water, thus:—

$$C_3H_5OH + H_2 = C_3H_6 + H_2O.$$
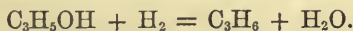
Aluminic allylate, some of which must have been formed, could not be isolated by the distillation *in vacuo* of the non-gaseous products of this reaction. Little, however, of this compound may have existed at any moment, for as soon as any appreciable quantity of water had been formed by the hydrogenisation of the hydroxyl group of the alcohol, the reagents may have acted upon the water then present in preference to the alcohol.

Phenyl, Cresyl, and Thymol Alcohols.—Aluminium in presence of aluminium iodide, very rapidly decomposes these compounds at 100°, hydrogen being evolved equivalent to the metal employed, and aluminic phenylate, cresylate, or thymolate formed. The aluminium compounds cannot be obtained in a pure state by distillation *in vacuo*, but on heating the respective alcohols to about 200°, with the theoretical amount of aluminium, and enough iodine to start the action, and pouring off the semi-fluid product, they were obtained approximately pure. Thus a specimen of the phenylate prepared as described gave on analysis 9·49 per cent. of aluminium, the calculated being 8·97; a

specimen of cresylate 7·57, the calculated being 7·89; and a specimen of thymolate 5·96, the calculated being 5·79.

The phenylate hardens as it cools, whilst the cresylate and thymolate remain plastic for some considerable time.

Aluminium itself when boiled with phenyl and cresyl alcohols, very slowly decomposes them, phenyl alcohol being the more readily acted upon. Thymol does not appear to act at all on the metal, when boiled with it.

Benzyl Alcohol.—The hydrogen in this alcohol is also replaced by aluminium in presence of aluminium iodide. The action is very violent, the greater part of it being over in a few seconds. The aluminium compound undergoes complete decomposition on heating *in vacuo.*

Aluminium alone has no action on this compound, but aluminic iodide readily decomposes it on gently heating, an organic iodide having a violent action on the eyes and skin—probably benzylic iodide —being produced.

Naphthol.—At a temperature between its melting and boiling points, this alcohol is acted on by aluminium alone, hydrogen being evolved equivalent to the metal. The aluminic naphtholate, as in the case of the phenol compounds, does not distil *in vacuo.* The naphthol used was the β-naphthol, melting at 121—122° C.

Alcohols of other Atomicities.

Ethylene Alcohol.—When a solution of aluminic iodide in this alcohol was heated to a little above 100°, the mixture turned brown, and at about 160° a few bubbles of gas were produced containing an olefine. When heated to a higher temperature, a liquid having a lower boiling point than the alcohol was formed, which, from its action upon potassium and anhydrous copper sulphate, was concluded to be water. When heated with Al_2I_6 and aluminium or aluminium and free iodine, little or no difference was noticed in the action until the liquid referred to, collecting in the tubule of the condenser, fell into the flask, when after each drop a few bubbles of gas escaped, probably hydrogen, from its decomposition. We conclude, therefore, that the basic hydrogen of this alcohol is not replaced by the reagents employed.

Propenyl Alcohol (Glycerol).—Aluminic iodide dissolves somewhat slowly in this compound, but when the mixture is heated to about 140°, both substances undergo decomposition, aluminic hydrate, free iodine, and an oily body having the properties of allyl iodide being produced. The reaction doubtless accords with the equation :—

$$2C_3H_5(HO)_3 + Al_2I_6 = Al_2(HO)_6 + 2C_3H_6I + I_4,$$

from which it would follow that were the substances heated in presence of metallic aluminium, the sole products of the chemical change would be aluminic hydrate and allyl iodide.   The experiment, details of which follow, show that this is the case :—

4 grams of aluminium iodide, and 2 grams of aluminium foil were heated with 30 c.c. of dry glycerine* until the reaction was completed.

Hydrogen was not evolved nor any other gas.   On further heating the product, 1·2 c.c. of the organic iodide distilled. The residue, being now almost solid, 30 c.c. of glycerol were added to it, and again heated, when 1·5 c.c. more of the iodide passed over, which together with the first portion, approximates very closely to the calculated amount.

Dr. Hodgkinson, working on the lines of our paper already referred to, has also obtained allyl iodide, and almost in amount corresponding to the iodide employed, by heating glycerol with aluminium and free iodide (*Chem. News*, 1877, p. 237).

General Properties.

The aluminic alcohols are non-crystalline, and solid at the ordinary temperature, and those obtained pure are yellowish-white in colour. They are all more or less decomposed on heating at the ordinary atmospheric pressure, but those of the methyl series distil at reduced pressures, affording the first examples of organic compounds containing both oxygen and a metal capable of distillation.†   The solubility in alcohol, ether, and benzol, of those which have been obtained pure, are roughly indicated in the annexed table :—

Aluminic compound.	In alcohol.	In ether.	In benzol.
Ethylate.	Nearly insoluble.	Slightly.	Moderately.
Propylate.	Very slightly.	Slightly.	Moderately.
Butylate.	Moderately.	Very.	Very.
Amylate.	Moderately.	Moderately.	Very.

The aluminium-compounds of the methyl series possess in a marked degree the property of remaining fluid below their fusing points. Thus specimens of ethylate and butylate, which melted at 130° and 140° respectively, remained fluid at 70° for at least an hour; and a

* Obtained by bubbling hydrogen through the liquid heated to 160° for three days.

† In 1877 Conrad showed that another aluminic compound, $C_{18}H_{27}O_9Al$, and an analogous copper salt, are capable of distillation (*Liebig's Ann.*, **188**, 272).

specimen of amylate which melted at 70° remained fluid for days at the ordinary temperature. The propylate decomposes somewhere near its melting point, which was found to be about 60°. Another peculiarity of these bodies is that they solidify first into a transparent, or semi-transparent mass, but after the lapse of some days, they become opaque. The numbers given as the melting points we regard only as approximations, for different specimens of some of these compounds, especially the amylate, have been found to differ in this respect.

The specific gravities of the compounds at 4° C., were found to be, for the—

Ethylate,   1·147
Propylate, 1·026
Butylate,   0·9825
Amylate,   0·9804.

The action of water upon the ethylate was found to give aluminic hydrate and alcohol :—

$$Al_2(C_nH_{2n+1}O)_6 + 6H_2O = 6(C_nH_{2n+1}OH) + Al_2(OH)_6.$$
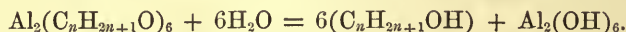
The ease with which the positive radical of the water, in this latter (probably typical) action, combines with the negative radical of the aluminic alcohols, points to a great number of probable syntheses; and from the atomicity and other chemical qualities of aluminium, it is very probable that compounds of very considerable interest will result therefrom.

Theoretical Note.

We have offered two possible explanations of the part which the relatively small quantity of aluminic iodide plays in these aluminium substitutions. The one for which we expressed a preference, as already mentioned, was the one requiring the formation of hydriodic acid in the first step of the reaction. No direct evidence, however, of the production of this substance was found until our experiments with the phenyl group of alcohols, when, on gently warming each of these compounds with aluminic iodide, an appreciable quantity of hydriodic acid was evolved. This matter is more fully discussed in our paper on the aluminium-iodine reaction in the *Proceedings of the Royal Society.*

ALUMINIUM ALCOHOLS. Part II. THEIR PRODUCTS OF DECOMPOSITION BY HEAT.

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WE lately described some alcohols in which the basic hydrogen is replaced by aluminium (*Chem. Soc. J.*, 1876, p. 158; 1881, p. 1; *Proc. Roy. Soc.*, 1880, p. 546). We have also observed (*Proc. Roy. Soc.*, 1880, p. 548) that these compounds are decomposed by heat, and that in two ways: they may split up into alumina and the alcohol and olefine, or into alumina and the ether. The further investigation of this matter forms the subject of the present paper.

Ethyl Series.

The effect of heat on the aluminic ethylate has already been partially described. Although the compound may be distilled *in vacuo*, it is almost wholly broken up near its boiling point under the ordinary pressure of the atmosphere. A little ether is formed, but the decomposition takes place almost entirely into ethene, alcohol, and alumina, thus:—

$$(C_2H_5O)_6Al_2 = Al_2O_3 + 3C_2H_4 + 3C_2H_6O.$$
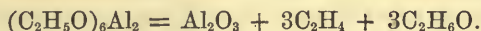
In the case of the amylate, a similar decomposition occurs, but the yield of amylic ether is somewhat greater.

Phenyl Series.

If similar reactions take place with the aluminic alcohols of the phenyl series, we should obtain the simple ethers $(C_nH_{2n-7})_2O$, only one of which has been described, together with the hydrocarbons, C_6H_4 and C_7H_6, and their homologues. We therefore studied more completely the action of heat upon the aluminium derivatives of certain of the phenyl alcohols.

Aluminium Phenylate.

469 grams of this compound were heated in a flask fitted with a wide bent tube about 16 inches long. The substance quickly melted, and, after a little free phenol had passed over, a somewhat viscid yellowish-brown liquid distilled. The residue consisted of charcoal, tarry matter, and alumina. The distillate weighed 268 grams, and after redistillation to remove a small quantity of aluminium phenylate

which was carried over, there remained 252 grams. This was separated by fractionation into three portions :—

> a.   52 grams, from about 80—200°.
> b.   160 grams, from 200—280°.
> c.   34 grams, above 280°.

Fraction a.—The greater part of this portion distilled between 178° and 184°, a small quantity of a very mobile liquid of the odour of benzene passing over at about 80°. By repeated distillation of this higher boiling point product, and rejecting small portions above 180°, a considerable part of it was obtained boiling between 178° and 180°. This liquid was colourless ; it was soluble in a solution of potash, crystallised on cooling in long needles ; gave hydrogen with the aluminium-iodine reaction, and, on combustion with oxide of copper, yielded 76·57 per cent. of carbon and 6·79 of hydrogen. The principal part of this fraction consisted, therefore, of phenol.

Fraction b.—This portion was shaken repeatedly with three or four times its volume of boiling water to remove any phenyl alcohol not separated by distillation. The residual oily liquid was dried over calcium chloride, and subsequently distilled several times, each time rejecting whatever failed to pass over below 300°. The distillate was now quite colourless, and nearly the whole of it boiled constantly at 249°.

This substance was not miscible with water or aqueous potash, and did not yield hydrogen by the aluminium-iodine reaction. It separated from an alcoholic solution, on cooling to a low temperature, in colourless prisms. Its specific gravity was 1·0904.

Burnt with oxygen and copper oxide—

> I. 0·3658 gram gave 1·1320 gram CO_2 and 0·1955 H_2O ;
> II. 0·4241   ,,   ,,   1·3175 gram CO_2 and 0·2279 H_2O ;

results which appear from the following comparison to agree with the formula $C_{12}H_{10}O$, which is that of *phenyl ether*, described by Hoffmeister in 1871 (*Ber.*, **3**, 747).

			I.	II.
C_{12}	144	84·70	84·40	84·72
H_{10}	10	5·88	5·93	5·97
O	16	9·42	—	—
	170	100·00		

Its index of refraction for A was 1·5675 at 25°, and the length of the spectrum, from A to H, was 0·0583. Two determinations gave 90·05 and 90·22 as the refraction equivalent for A, which accords with theory.

Portions of this compound were found to solidify to a mass of colourless prismatic crystals, while other portions apparently identical remained liquid. A few experiments were made in the hope of elucidating this anomaly. A quantity of the freshly distilled compound was well shaken in a stoppered bottle. No solidification occurred. A crystal of the substance was now introduced, and immediately beautiful star-shaped crystals formed on several parts of the introduced crystal, others forming on these, and the whole liquid speedily passed to the crystalline condition. This change was accompanied by a rise in temperature of 8°. Another portion of the substance remained liquid at 2° for hours, but quickly solidified on the vessel containing it being immersed in a freezing mixture.

Fraction c.—This portion consisted of a viscid brown liquid, containing grains of a yellow solid. It was distilled a number of times, rejecting each time a small quantity of a non-volatile tarry substance. The distillate was now less viscid and much lighter in colour. On slowly distilling it, an almost colourless liquid passed over at about 280°, which condensed to a nearly white solid; and this was followed at a higher temperature by a comparatively small quantity of a non-crystallisable, thick orange-coloured liquid.

The solid was purified by repeated solution in, and crystallisation from, alcohol of sp. gr. 0·880. It was white in colour, soluble in absolute alcohol, and more so in ether. It melted at 97°, and sublimed slowly a little below this temperature.

On combustion with oxygen and copper oxide after drying at 100°:

$$\text{I. } 0·1275 \text{ gram gave } 0·4018 \text{ } CO_2 \text{ and } 0·0654 \text{ } H_2O$$
$$\text{II. } 0·1268 \quad ,, \qquad ,, \quad 0·3987 \text{ } ,, \quad ,, \quad 0·0646 \text{ } H_2O$$
$$\text{III. } 0·1933 \quad ,, \qquad ,, \quad 0·6099 \text{ } ,, \quad ,, \quad 0·1005 \text{ } H_2O.$$

The third portion (III) analysed had undergone sublimation. The results expressed in parts per 100 give—

	I.	II.	III.
C	85·94	85·75	86·03
H	5·70	5·66	5·77

On the determination of its vapour-density by the method of Victor Meyer—

0·0978 gram gave vapour = in volume 12·04 c.c. (corr.)
0·0836   ,,   ,,   10·19   ,,

These data give 181·4 and 183·0 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $C_{13}H_{10}O$.

			Calc. for 100 pts.	Found (mean).
C_{13}	....	156	85·71	85·91
H_{10}	....	10	5·50	5·71
O	....	16	8·79	—
		182	100·00	

Three compounds of this formula have been described—fluorene alcohol, and diphenyl ketone, and its isomer. Our body does not accord in physical properties with the description of any one of these compounds. We are inclined, however, from the mode of its formation, to regard it as a phenyl ketone.

It would appear, then, from these results:—

1st. That about half of the phenylate was resolved by heat into phenyl ether and alumina, thus—

$$(C_6H_5O)_6Al_2 = Al_2O_3 + 3(C_6H_5)_2O,$$

which action gives a simple method of preparing this ether.

2nd. That a compound of the formula $C_{13}H_{10}O$ was formed in relatively small quantity.

3rd. That about one-quarter of the aluminium compound was resolved very probably in accordance with the equation—

$$(C_6H_5O)_6Al_2 = Al_2O_3 + 3C_6H_6O + 3C_6H_4.$$
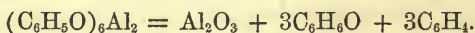
No evidence was found of the existence of the hydrocarbon C_6H_4, shown in this scheme, but it is not improbable that it existed in admixture in that portion of the distillate above 300°, which was richer in carbon than any of the bodies separated; in fact it contained 87·5 per cent., and its specific refraction and dispersion were very high.

Aluminium Para-cresylate.

760 grams of aluminium para-cresylate were heated as in the case of the phenylate. The distillate was almost solid when cold, yellowish-brown in colour, and weighed 463 grams. This product was boiled with 6 litres of alcohol, sp. gr. 0·805, and filtered from alumina by a calico strainer, supported in a hot water funnel. On cooling, a yellow crystalline substance separated, which, after washing with 9 litres of alcohol, weighed when dry 71 grams. This body was dissolved in alcohol, and crystallised therefrom, until the menstruum was free from yellow colour. After drying at 100°, the body was burnt with oxygen and copper oxide.

I. 0·1622 gram gave 0·5097 gram CO_2 and 0·0956 gram H_2O.

This substance was, however, still yellow, and when melted exhibited a blue fluorescence. It was slowly distilled, when nearly the

whole passed over at 307°. The distillate was of the colour of pale hock, free from the blue fluorescence, and solidified on cooling to a cream-coloured crystalline mass. This was dissolved in boiling alcohol, from which solution the substance separated on cooling in very thin plates, white in colour, and of a pearly lustre.

On combustion—

II. 0·1619 gram gave 0·5081 gram CO_2 and 0·0989 H_2O.

The substance permitted of sublimation, and by the following method was obtained in long white lustrous plates. The compound in the condition of the white plates was melted and poured into a porcelain boat, and placed in the forepart of a glass tube about $1\frac{1}{2}$ inch in diameter, through which a current of hydrogen was passing. The part of the tube in proximity to the loaded boat was heated, and the boat and the flame slowly moved backwards as the compound sublimed.

On combustion—

III. 0·1205 gram gave 0·3774 gram CO_2 and 0·0717 gram H_2O.

These results expressed in parts per 100 give—

	I.	II.	III.
C	85·70	85·59	85·70
H	6·54	6·78	6·52

On the determination of its vapour-density—

0·1186 gram gave vapour = in volume 12·64 c.c. (corr.)
0·1179   ,,   ,,   ,,   12·60   ,,

These determinations were made in hydrogen, and give 209·4 and 208·8 respectively for the molecular weight of the substance. The most probable molecular formula of the compound is therefore $C_{15}H_{14}O$.

		Calc. for 100 pts.	Found (mean).
C_{15}	180	85·71	85·66
H_{14}	14	6·66	6·61
O	16	7·63	—
	210	100·00	

It melted at 168°, and dissolved but slightly in alcohol, giving 2·5 per cent. at the boiling temperature, and 0·4 per cent. at 20°.

The alcoholic liquids obtained in the operations just described were distilled. About 10 grams of the solid compound separated, and after the alcohol had passed over, the residual liquid began boiling at 190°, gradually rising beyond the limits of the thermometer. The greater part however (120 grams) distilled between 190° and 300°. This

fraction was digested with successive portions of aqueous potash, and the alkaline liquid subsequently neutralised with hydrochloric acid. 36 grams of an oily brown liquid separated, which, after washing with a little water, and drying with calcium chloride, boiled for the most part between 199° and 202°. This distillate was colourless, and had the composition, refraction, and other physical and chemical qualities of para-cresol.

The portion of the fraction not soluble in aqueous potash was of a dark, yellowish-brown colour. It was washed with water, and digested with calcium chloride. It was now distilled about thirty times, each time rejecting small portions above 300°, and below points gradually rising from 220—270°. The distillate was colourless at this stage, and on cooling to a low temperature, formed a semi-fluid mass containing colourless prismatic crystals. This product was dissolved in about twice its volume of warm alcohol, from which solution, on cooling to a low temperature, the substance separated in prisms. It was dried at 100°, and burnt with copper oxide.

I. 0·1070 gram gave 0·3324 CO_2 and 0·0710 H_2O.
II. 0·0942 „ „ 0·2928 „ „ 0·0597 „
III. 0·1541 „ „ 0·4793 „ „ 0·0972 „

These results expressed in parts per 100 give—

	I.	II.	III.
C	84·72	85·30	84·82
H	7·37	7·04	7·00

On the determination of its vapour-density—

0·1077 gram gave vapour = in volume 12·13 c.c. (corr.).
0·1040 „ „ „ 11·75 „

These numbers give 198·1 and 197·6 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $C_{14}H_{14}O$—

		Calculated.	Found (mean).
C_{14}	168	84·84	84·94
H_{14}	14	7·07	7·13
O	16	8·09	—
		100·00	

which would be that of cresyl ether, and from the general analogy between it properties and mode of preparation and that of phenyl ether, little doubt can exist as to the compound being the second ether of the phenyl series. As it was obtained through the aluminium derivative of para-cresylate, we name the compound *para-cresyl ether*.

This compound melts at 50° C., is very soluble in ether and in benzol, moderately so in alcohol, and has an odour resembling that of phenyl ether, but fainter.

The action of heat on aluminium cresylate, as was to be expected, presents a general similarity to the action of the same agent on the analogous phenyl compound. The points of difference in the two cases are to be found in the variations in the amount of the corresponding compounds produced. The aluminium phenylate, for example, yields a relatively large quantity of phenyl ether, while the cresyl-aluminium alcohol gives only a relatively small quantity of the corresponding compound. Again, the phenyl compound yields only a small quantity of the $C_{13}H_{10}O$ body, while the cresyl compound yields a relatively large quantity of the homologue $C_{15}H_{14}O$. The hypothetical hydrocarbon C_7H_6 has not been found.

Aluminium Thymolate.

1000 grams of this compound were heated as in the cases of the analogous phenyl and cresyl compounds. A little free thymol at first passed over, then an orange viscid liquid, which partially solidified on cooling. As soon as the thymolate became fluid by heat, it was noticed to be in violent commotion, evidently from the passage through it of gas. The nature of this gas, and the meaning of its evolution, were determined.

45 grams of thymolate were heated until gas evolution practically ceased. The gas for the first 3240 c.c. was a pure olefine, after which it consisted of a mixture of the olefine and probably marsh-gas, the latter compound being evolved in an increasing ratio towards the completion of the action. The total gas collected (corr.) measured 5856 c.c., of which 5032 c.c. combined with bromine.

In another experiment, employing 230 grams of thymolate, 196 grams of an olefine bromide were obtained. The greater part of this compound boiled, on rectification, between 136° and 139°. Its sp. gr. at 4° was 1·913, and when dissolved in alcohol and treated with zinc it gave zinc bromide and a gas burning with very luminous flame. The gas set free on heating the fluid thymolate is therefore propylene.

The distillate from the 1000 grams of thymolate weighed 470 grams. It was divided by distillation into two portions:—a, which passed over below 280°, and b, above that temperature.

Fraction a.—This portion was liquid, of a brownish-yellow colour, and weighed 207 grams. It was treated with successive quantities of a warm solution of potash, in which it partially dissolved. The alkaline solutions obtained were neutralised with hydrochloric acid, when a

brownish oily liquid separated, which was dried over calcium chloride and distilled. The distillate was redistilled some five or six times, each time rejecting the portion not passing over below 205°. The distillate at this stage was colourless, and nearly the whole of it distilled between 196—202°.

On combustion with copper oxide and oxygen—

0·1820 gram gave 0·5164 gram CO_2 and 0·1208 gram H_2O.

The substance gave hydrogen with the aluminium reaction, and readily dissolved in aqueous potash. Its refractive index for A was 1·5316 at 23° C. These qualities, jointly with its composition exhibited in the following comparison, show the compound to be cresol:—

	Calculated.	Found.
C_7	77·77	77·38
H_8	7·40	7·37
O	14·83	15·25 (by diff.)
	100·00	

Moreover, as this substance did not solidify at a temperature of −17° C., we concluded that it is meta-cresol. Hitherto this modification had not been seen in the solid condition, but on stirring the product just described with a thermometer, it underwent solidification at −14° C.

Fraction b.—This portion consisted apparently of a yellow crystalline body in admixture with a brownish viscid liquid. It weighed 231 grams. After the addition to it of the high boiling portion of fraction *a*, the product was mixed with about twice its volume of ether, and the mixture heated for a few minutes in hot water. On cooling in a freezing mixture the brown liquid remained in solution, while the solid was apparently unaffected. The solid was now washed on a filter with cooled ether. It quickly became white, and was then found to weigh 15 grams, and to consist of small shining scales. This body was next dissolved in boiling alcohol, sp. gr. 0·805, from which solution, on cooling, it separated in large white plates, having a pure pearly lustre. It was dried and burnt with copper oxide and oxygen with the following results:—

I. 0·1917 gram gave 0·6017 gram CO_2 and 0·1142 gram H_2O.
II. 0·2035   „   0·6383   „   0·1218   „

These data expressed in parts per 100 give—

	I.	II.
C	85·60	85·54
H	6·61	6·65

On the determination of its vapour-density—

    0·1279 gram gave vapour = in volume to 13·66 c.c. (corr.).
    0·1219   ,,   ,,   ,,   13·04   ,,

These numbers give 209 and 208·6 respectively for the molecular weight of the compound. Its molecular formula is therefore $C_{15}H_{14}O$—

		Calc. for 100 pts.	Found (mean).
C_{15}.............	180	85·71	85·57
H_{14}	14	6·66	6·63
O	16	7·63	—
	210	100·00	

This compound permits of sublimation by the method used for the compound of the same molecular formula from para-cresol. It sublimes, however, much more readily, and forms larger crystals than that substance.

The ethereal liquids, obtained in the operation described, were distilled. The residuum, after the ether had separated, commenced distilling at about 250°, from which temperature to 300° an almost colourless liquid passed over. The portion above 300°, after distillation, was treated with about twice its volume of ether. On standing, more of the $C_{15}H_{14}O$ compound separated, and by distilling the ethereal solution itself, another quantity of liquid was obtained, boiling between 250° and 300°. These operations were performed on the residue boiling above 300° until no more of the solid compound separated.

All the liquid obtained between 250° and 300° was now treated with a hot solution of potash, then washed with water, dried over calcium chloride, and distilled. The liquid commenced boiling at about 270°. It was distilled some 40 times, each time rejecting small quantities boiling above 300°. The liquid had now a faint yellow tinge, and boiled for the most part between 284° and 288° C. Its index of refraction for a was 1·5576 at 16° C. Burnt with oxygen and copper oxide—

    I. 0·1500 gram gave 0·4676 gram CO_2 and 0·0963 gram H_2O.
    II. 0·1765   ,,   0·5488   ,,   0·1136   ,,

These results expressed in parts per 100 give—

	I.	II.
C	85·01	84·80
H.................	7·13	7·15

On the determination of its vapour-density—

    0·0929 gram gave vapour = in volume to 10·68 c.c. (corr.).
   0·1176   ,,   ,,   ,,   13·56   ,,

These numbers give 194·16 and 193·58 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $C_{14}H_{14}O$—

		Calc. for 100 pts.	Found (mean).
C_{14}	168	84·84	84·91
H_{14}	14	7·07	7·14
O	16	8·09	7·95 (by diff.)
	198	100·00	100·00

which is that of cresyl-ether. The physical properties of this substance, however, differ materially from those of the cresyl-ether discovered among the products of the aluminium para-cresylate. For example, it does not solidify even in a freezing mixture, or crystallise from alcohol. We are disposed therefore to regard it as isomeric with the ether of para-cresol, and from the mode of its formation to name it *meta-cresyl-ether.*

It appears then that heat readily resolves aluminium thymolate into aluminium meta-cresylate and propylene, thus—

$$Al_2(C_{10}H_{13}O)_6 = Al_2(C_7H_7O)_6 + 6C_3H_6,$$
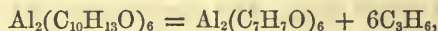
and further, that the same agent splits up the aluminium compound so produced into alumina, meta-cresol, meta-cresyl-ether, and the pearly compound $C_{15}H_{14}O$, which, judging from the want of agreement between the physical properties of this substance and the one of the same molecular formula from the para-cresylate, would appear to be isomeric with this latter compound. The points of difference referred to are set out in the table below :—

	Melting point.	Solubility in abs. alcohol		Solubility in benzol 21° C.
		Boiling.	20° C.	
$C_{15}H_{14}O$ from para-cresylate	168°	2·5 p. c.	0·4 p. c.	3·3 p. c.
$C_{15}H_{14}O$ from meta-cresylate (thymolate)	200	1·0 ,,	0·17 ,,	0·93 ,,

Both of these substances are alike in one special particular, that of giving out a bluish-white light when shaken or rubbed.

Two substances of the formula $C_{15}H_{14}O$ have already been described, viz., para-ditolyl and di-benzyl ketones. Our compounds do not accord in physical properties with either of these bodies. From the composition and mode of formation we are, however, inclined to regard them as ketones, and provisionally as para- and meta-cresyl ketones respectively.

Aluminium β-Naphthylate.

150 grams of β-naphthol were heated with 10 grams of aluminium until the evolution of hydrogen nearly ceased. Some of the metal remained in the free condition, which is doubtless to be attributed to the infusible character of the resulting naphthylate preventing the completion of the action.

On distilling the mixture of naphthol and naphthylate a reddish-brown viscous liquid was obtained, which solidified on cooling. It was divided by distillation into two portions:—*a*, which passed over below 300°, and *b*, above this temperature.

Fraction a weighed 40 grams, and consisted of naphthalene and naphthol in about equal proportions.

Fraction b.—This portion was solid and dark yellowish-brown in colour. It was dissolved in boiling alcohol, and the yellow crystalline substance, which separated as the solution cooled, again and again crystallised from the same liquid. This product was next dried and twice distilled, which it did at a temperature above the limits of the thermometer. On cooling, the distillate formed a crystalline mass pale yellow in colour. It was crystallised from boiling alcohol until the menstruum was free from colour. The substance now separated from alcohol in thin pearly white rhomboidal plates. It melted at 104° C., and on combustion—

I. 0·2713 gram gave 0·8837 CO_2 and 0·1268 gram H_2O.
II. 0·2874 „ 0·9359 „ 0·1354 „

These results expressed in parts per 100 give—

	I.	II.
C	88·83	88·81
H	5·19	5·23

On the determination of its vapour-density—

0·1219 gram gave vapour = in volume 10·16 c.c.
0·1341 „ „ „ 11·02 „
0·1399 „ „ „ 11·64 „

These numbers give 267·8, 271·4, and 268·7 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $C_{20}H_{14}O$—

		Calculated.	Found (mean).
C_{20}	240	88·84	88·82
H_{14}	14	5·18	5·21
O	16	5·98	5·97 (by diff.)
	270	100·0	

which would be that of a naphthyl ether. As the body was formed by the decomposition of the β-naphthylate we name it provisionally *β-naphthyl ether*.

The alcoholic liquids obtained in the operations just described were distilled. After the alcohol had passed over the residuum commenced boiling at 290°, but quickly rose beyond the limits of the thermometer. A dark-brown viscous liquid distilled. This dissolved readily in alcohol, and the resulting solution very slowly deposited a quantity of the solid body just described. When this body had ceased separating a comparatively small quantity of a very viscous substance was obtained on distillation, containing 89·5 per cent. carbon and 5·3 per cent. hydrogen. It freely dissolved in alcohol, the solution exhibiting a blue fluorescence.

On distilling the several highest boiling point portions collected in the above operations a semi-solid distillate was obtained, which on treatment with boiling alcohol left a dark-yellow crystalline substance. This separated from benzene in square dark golden-yellow shining plates. It dissolved very slightly in alcohol, to which a mere trace imparted a powerful blue fluorescence. The quantity obtained was too small to determine its molecular formula, but a combustion showed it to be a very highly carbonaceous hydrocarbon, probably contaminated with a small quantity of an oxygenated body. For future reference we propose, from its double colour, the temporary name of chrysendiene.

The principal product of the decomposition by heat of β-aluminium naphthylate is β-naphthyl ether, thus :—

$$(C_{10}H_7O)_6Al_2 = Al_2O_3 + 3{C_{10}H_7 \atop C_{10}H_7} \Big\} O.$$
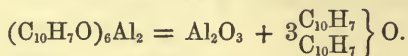
Aluminium-α-Naphthylate.

In order for aluminium to replace the basic hydrogen in α-naphthol the usual quantity of iodine must be employed. This difference between the α- and β-modification serves to discriminate the two naphthols.

520 grams of α-naphthylate were prepared in the manner ordinarily used for the aluminium-derivatives of the other alcohols. This compound underwent decomposition on heating, but the temperature required was much higher than in the case of the analogous β-compound. A brownish-yellow viscous liquid distilled, which solidified on cooling, and weighed 319 grams. This product was separated by distillation into two portions: *a*, which passed over below 310°, and *b*, above this temperature.

Fraction a weighed 90 grams, and mainly consisted of naphthalene.

Fraction b.—This was melted and poured into about twice its volume of boiling alcohol. A quantity of a yellow substance remained undissolved, and a little more separated on the cooling of the alcoholic liquid. These operations were repeated four times on the yellow body successively obtained. The substance was now distilled, and on cooling the distillate solidified to a yellow crystalline mass. This was crystallised some four times from benzene, in which it dissolved more readily than in alcohol. It now separated in large shining rhombic plates of the colour of uranium glass. Burnt with copper oxide—

I. 0·2694 gram gave 0·9302 gram CO_2 and 0·1342 gram H_2O.
II. 0·2816 ,, 0·9741 ,, 0·1408 ,,

These results expressed in parts per 100 give—

	I.	II.
C	94·17	94·34
H	5·53	5·55

On the determination of its vapour-density—

0·1026 gram gave vapour = in volume to 9·06 c.c.
0·1029 ,, ,, ,, 9·06 ,,

These numbers give 253·0 and 253·4 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $C_{20}H_{14}$.

		Calculated.	Found (mean).
C_{20}	240	94·43	94·26
H_{14}	14	5·57	5·54
	254	100·00	99·80

Three compounds of this formula are known, viz., $\alpha\alpha$-, $\alpha\beta$-, $\beta\beta$-dinaphthyls. The substance described resembles in physical properties the $\beta\beta$-dinaphthyl of Mr. Watson Smith. It dissolves in hot oil of vitriol, forming a light green, and subsequently a blue colour, and melts at 189°.

The residue left after distilling off the benzene from the liquids obtained in the purification of the hydrocarbon just described was boiled with alcohol, in which the greater part dissolved. On cooling a substance separated, which, after many crystallisations, formed long flat buff-coloured needles. When burnt with copper oxide it gave, as the mean of two determinations, 90·8 per cent. carbon and 5 per cent. of hydrogen. And two determinations of its vapour-density gave for mean 132·6. It would appear from these results that the substance is not a single compound. We are inclined to regard it in fact as

consisting of a $C_{20}H_{14}O$ or $C_{21}H_{14}O$ body in admixture with di-naphthyl.

The alcoholic liquids from fraction b were distilled.   After the alcohol had passed over a brown viscous substance distilled, containing 90·38 per cent. of carbon and 5·21 per cent. of hydrogen.   It dissolved readily in alcohol, the solution exhibiting a blue fluorescence.

The action of heat on the two aluminium naphthylates is seen to be very different.   The β-compound splits up at a lower temperature than does the α, and yields as the principal product naphthol-ether, while it is doubtful whether an ether is formed at all in the case of the α-compound.

Though these aluminium alcohols are more or less distillisable at reduced pressures, they are alike decomposed by heat at the ordinary pressure of the atmosphere.   The products of the decomposition of the series $C_nH_{2n+1}OH$, $C_nH_{2n-7}OH$, and $C_nH_{2n-13}OH$, appear, however, to be somewhat different.   The first series yields the corresponding ethers, alcohols, and olefines ; the second, the corresponding ethers and alcohols (with the exception of the thymolate, which suffers re-duction to cresylate in the first stage of the action), together with crystalline bodies hitherto undescribed, and probably consisting of ketones.   The third series gives in one case the corresponding ether and probably alcohol, together with hydrocarbons of a class differing from the olefines.

LABORATORY NOTES.

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.,
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I. ON THE ACTION OF LIGHT AND HEAT ON CANE AND INVERT SUGARS.

NOTHING is more familiar to chemists than that living yeast-cells, and some other vegetable structures, are capable of resolving cane-sugar into alcohol and carbonic anhydride; and this decomposition is the more interesting as all attempts to bring it about by known chemical or physical processes have hitherto failed. We thought it worth while to try the effect of the copper-zinc couple at the ordinary temperature. The reaction did not take place in a 5 per cent. solution of cane-sugar: hydrogen was of course evolved (from the water), but no carbonic anhydride. At 100° C., however, carbonic anhydride was slowly evolved, and a small quantity of liquid distilled over, which gave iodoform on treatment with iodine and potassium hydrate, and acetic acid on treatment with potassium chromate and sulphuric acid. Our hopes appeared to be realised, but on examining the chemical change more fully, we found that the carbonic anhydride did not come from the sugar at all, and that the organic substance which distilled over was not alcohol, and was not dependent upon the couple for its formation. In fact, the carbonic anhydride arose from the splitting up of oxicarbonate of zinc, which is formed in the washing of the couple, and of which we had no previous knowledge; while the organic body is a product of the action of heat upon the sugar solution.

While investigating this subject, we made various observations regarding the influence of heat, light, germs, and air upon solutions of cane and altered sugar (glucose), and as they may help to clear up some of the contradictory statements that have been made upon this subject, we are induced to record the most important of them.

1. *The Action of Heat on an Aqueous Solution of Cane-Sugar.*

The usual mode of experimenting was to take a number of tubes with narrow tubules, of about 20 c.c. capacity, and nearly fill them with a solution of pure cane-sugar (5 grams to 100 c.c. of distilled water), which was then boiled for about five minutes in an oil-bath. To determine the effect of heat in absence of air, some of the tubes were sealed while the liquid was still boiling. About 15 c.c. of the solution in a sealed tube were exposed for 14 days to a temperature of 90° to 95° C.; it slowly became of a pale yellow colour, and was found to contain 3·6 per cent. of glucose, was acid to test-paper, and, on distillation, the iodoform-producing substance was detected. In another experiment the heating was prolonged to six weeks; the solution became much darker in colour, and contained some yellowish-brown matter, which readily dissolved in a solution of potassium hydrate, from which it was again precipitated on the addition of an acid. The solution was slightly acid, contained 2·8 per cent. of glucose, and yielded the iodoform-producing compound. It would appear, then, that nothing but an elevated temperature is necessary to convert an aqueous solution of cane-sugar into glucose and an acid body, with a minute quantity of an unknown volatile substance.

Experiments were made to ascertain whether the iodoform-yielding body is produced immediately from glucose, and whether carbonic anhydride accompanies its formation. 400 c.c. of a 5 per cent. solution, prepared carefully by ourselves, were boiled in a retort, and the distillate tested from time to time, and the substance we were in search of was detected in successive portions of the distillate; boiling water was added to the residue to make up the volume, and the air was driven out of the apparatus by a stream of pure hydrogen. The slow boiling was continued for 12½ hours, hydrogen passing through the apparatus, and subsequently through tubes containing baryta-water; the distillate contained, as before, a small quantity of the volatile compound, but no carbonic anhydride. It is evident, therefore, that the chemical reaction is essentially different from a vinous fermentation, and that the iodoform-yielding compound is not alcohol is also proved by its totally distinct odour, and the different volatility of its aqueous solution; it is not separated from water by potassium carbonate, and no other means have been found for its isolation.*

In our original experiments, in which the copper-zinc couple was heated to about 100° C. with cane-sugar solutions, only traces of

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* Mr. Horace T. Brown has drawn our attention to a paper "On the Electrolysis of Sugar Solutions" in this Journal of July, 1872. He mentions an iodoform-producing body, which was probably the one here described, as he subjected his solution of glucose to distillation.

glucose were ever produced, even after the action had continued for weeks. This agent therefore prevents the conversion, probably by neutralising or destroying the acid compound as quickly as it is produced. It is remarkable also that a solution of cane-sugar remains colourless apparently any length of time, when heated with the copper-zinc couple.

2. *Influence of Light, Atmospheric Germs, and Air.*

It seemed of interest to examine some of the conflicting statements in regard to the conversion of cane-sugar into glucose. A number of the tubes previously described were very nearly filled with a 5 per cent. solution. Twelve were sealed, while the solution was boiling, and six of them were exposed to full daylight at ordinary temperatures, the other six being kept in the dark. Six more were opened to the air, the tubules being plugged with cotton-wool, and three of them were exposed to daylight, and sometimes to the direct rays of the sun, the other three being kept in complete darkness. Six others were prepared with the tubules open, three being exposed to the light, and three kept in the dark. After allowing the whole of these tubes to remain from December, 1877, to May, 1879, the solutions were examined for glucose and fungoid growths. The amounts of glucose found in the several experiments, are shown in the subjoined table:—

Nature of Experiment.	Grams of Glucose in 100 c.c.						
	I.	II.	III.	IV.	V.	VI.	Mean.
Solution boiled in tubes, but not exposed to light, &c.	0·0162	0·0185	0·0162	0·0168	0·0209	—	0·0177
In sealed tubes.							
(i). Exposed to light	0·0187	0·0116	0·0193	0·0160	0·0145	—	0·0160
(ii). In darkness	0·0145	0·0250	0·0152	0·0232	0·0203	0·026	0 0207
In tubes plugged with cotton-wool.							
(i). Exposed to light	0·0203	0·0193	0·0261	—	—	—	0·0219
(ii). In darkness	0·0246	0·0272	0 0262	—	—	—	0·0260
In open tubes.							
(i). Exposed to light	0·0366	0·0225	0·0490	—	—	—	0·0360
(ii). In darkness	0·0214	0·0325	0·0354	—	—	—	0·0297

As the very method of preparing these solutions produces about as

much glucose as was found in the tubes 17 months afterwards, the above results show that neither light nor air, singly or jointly, changes cane-sugar in aqueous solution at the ordinary temperature.

As Rouet (*Compt. rend.* for 1871, p. 1049) states that a solution of 10 grams of white cane-sugar in 50 grams of water, enclosed in sealed tubes from which the air had been expelled by boiling the liquid, and exposed for five months to light, was found to be half-converted into glucose, we made four experiments with solutions of this strength; and obtained substantially the same results as before.

All the solutions in the sealed tubes were found to be perfectly bright, and free from fungoid growths, as were those in the tubes plugged with cotton-wool and exposed to daylight. On the other hand, all the solutions open to the air contained white matter at the bottom of the tube and fungoid filaments in the liquid. In the tubes that were plugged with cotton-wool, but kept in the dark, a smaller quantity of white matter—about a millimetre in diameter—was found at the bottom of the liquid in each case. A microscopical examination of the white matter was kindly made by Dr. Lionel Beale, who reported that "the fluid contained abundant evidence of living organisms—micrococci, bacteroid bodies, and mycelial filaments."

It would appear then that light is detrimental to development of fungoid growths in a solution of cane-sugar exposed to atmospheric air.

II. On Hydroxylamine.

In our experiments on the reduction of nitrates we thought it not improbable that hydroxylamine might be found, and were led to make an observation or two upon that substance.

The Nessler reagent behaves with an aqueous solution of it in apparently the same manner as with an aqueous solution of ammonia, provided there be not more than 0.0002 gram in 100 c.c. of water; but if the solution is stronger, the visible effect is very different. The results are shown in the following table:—

Hydroxylamine in 100 c.c.	Appearance.
0.0004 gram	Blackish-brown opacity.
0.002 ,, ...	Reddish precipitate, slowly becoming black.
0.01 ,, ...	Reddish precipitate, becoming black at once.
0.02 ,, ...	Black opacity and precipitate immediately.

It was found that the copper-zinc couple was capable of reducing the hydrochloride of this base. In an experiment 14 c.c. of an aqueous

solution, containing 0·006 gram of the hydrochloride, were poured on to a small quantity of the couple (made from 125 square centimetres of foil, wet with water). In 30 minutes hydroxylamine disappeared, and ammonia was found in its place.

III. RECOVERY OF IODINE FROM ORGANIC IODIDE RESIDUES.

In the course of our work on the preparation of zinc ethers, &c., quantities of various organic iodides have been obtained, too impure for use, and therefore only of value for their iodine. The process we have employed now for some time for the recovery of this element from such residues is as follows :—

In the first place we transfer the iodine of the organic iodide to zinc by pouring the residues on an excess of copper-zinc couple wet with water or alcohol, and allowing sufficient time for the transference to be completed. It is well to attach an inverted condenser to the vessel, for some iodides undergo decomposition very rapidly with evolution of much heat. The residue is then digested with hot water to dissolve the zinc iodide, and the iodine may be separated by any one of the well-known reactions. We adopt that of bleaching powder, which, when performed on a pretty large scale, yields about 95 per cent. of the iodine actually present.

IV. A RESIDUAL PHENOMENON OF THE ELECTROLYSIS OF OIL OF VITRIOL.

In our study of the electrolysis of oil of vitriol (*Chem. Soc. Trans.*, 1879), we noticed that gas continued to be evolved from both electrodes for days after connection with the battery had been broken. In one case, where the acid had been subjected to the current for 48 hours, the following amounts of gas were collected in the limbs of the Hoffmann apparatus at the undermentioned times :—

Time.	Limb where H had been evolved.	Limb where O had been evolved.
1 day.	0·5 c.c.	2·8 c.c.
2 days.	1·8 ,,	7·8 ,,
3 ,,	5·1 ,,	12·2 ,,
5 ,,	9·1 ,,	16·8 ,,
7 ,,	12·4 ,,	19·8 ,,
9 ,,	14·4 ,,	21·5 ,,
13 ,,	16·6 ,,	22·2 ,,

In the first experiment, where the taps of the apparatus were open, the evolution of gas took place only at the electrodes, but in the one just detailed, where the taps were closed, gas was also noticed rising

in the reserve tube and occasionally from the liquid beneath the electrode in the hydrogen limb. This generation of gas was thought at first to arise from some electrochemical action; but on examination the gas in both limbs was proved to be nothing but oxygen, which at once negatived this supposition. On experimenting further it was found that the addition of a very small quantity of water to the acid which had surrounded the anode produced an evolution of gas, also that gas was slowly liberated from a plate of platinum immersed in the acid, and much more copiously by the metal in a fine state of division. These properties will be recognised as belonging to Berthelot's persulphuric acid, the presence of which fully accounts for not only the gas evolution at the platinum electrodes, but also that from the liquid in the reserve tube.

V. On Alleged Tests for Alcohol.

In the first of these notes we have shown that the formation of iodoform is not a certain test for alcohol. About the time of our experiments Mr. Davy communicated a note entitled "A New Test for Alcohol," which depends upon the fact discovered by him that alcohol strikes a beautiful blue colour with a warm solution of molybdic anhydride in oil of vitriol. On trial we found that the so-called test for alcohol was merely a test for a reducing agent. The following substances, among others, were found to give the blue coloration to the molybdic solution: Ammonium sulphide, ferrous sulphate, sodium sulphite, and formic acid. But, as we were more particularly concerned in the detection of alcohol in the presence of possible small quantities of sugar, the action of this latter substance was tried upon the test, when it was found that one drop of a 2 per cent. solution produced the blue coloration most distinctly. In 1805 Grotthus studied the electrolysis of this very molybdic solution, and noticed a blue coloration at the kathode, where it is known that reduction takes place.

VI. Reaction of the Copper-zinc Couple on Nitric Oxide.

It has been pointed out by Graham and others that hydrogen in the occluded condition is much more chemically active than when in its ordinary gaseous state.

We have already suggested that hydrogen, immediately after its liberation from water by the action of the copper-zinc couple, becomes more or less completely occluded by the spongy copper which constitutes the negative element, and that the reducing property of the couple arises from the presence of hydrogen in the occluded state. In continuation of our work on this subject we made the following

experiments on the action of the couple in the presence of water on nitric oxide :—

(i.) 30 litres of the gas were passed in 7 hours over 2000 square centimetres of zinc foil coated with 18 grams of black spongy copper, the couple being wet with water.   0·037 gram of ammonia was produced.

(ii.) In another experiment 26 litres of nitric oxide were passed in about 5 hours over 2500 square centimetres of zinc foil, coated with 20 grams of copper; 0·05 gram of ammonia was produced.

The question was now suggested, does free nitrogen also hydrogenise to ammonia under similar circumstances?   Several prolonged experiments were made, but no evidence was obtained of the formation of ammonia.

VII. On the Reducing Action of Spongy Lead.

In our recent experiments upon lead and lead peroxide batteries we were desirous of ascertaining whether spongy lead perfectly free from hydrogen was capable of reducing such salts as nitrate and chlorate of potassium.   For this purpose spongy lead was prepared by precipitating the metal from the acetate by means of zinc, taking care that the salt was always in excess.   It is difficult to imagine that lead prepared in this way should contain any occluded hydrogen.   Nevertheless, it somewhat quickly reduced nitrate to nitrite of potassium. This action was found to be accelerated by heat, and to be retarded by the presence of sulphuric acid.   A minute quantity of ammonia was also produced, especially when sulphuric acid was present or a high temperature employed.

In each of the experiments, the results of which are set out in the following table, 50 grams of spongy lead were employed, and 200 c.c. of a 5 per cent. solution of nitre.   In experiments III and IV the nitre solution contained 1 per cent. of H_2SO_4.

Experiment.	Temperature.	Time.	Percentages (grams).	
			KNO_3.	NH_3.
I.	13°	1 hour.	0·38	0·00005
„	„	24 hours.	2·06	0·00015
„	„	48 „	2·43	0·00024
II.	50	1 „	0·74	0·002
III.	13	1 „	0 05	0·006
IV.	50	1 „	0·13	0·003

Spongy lead has no action on an aqueous solution of potassium

chlorate, but in presence of 1 per cent. of H_2SO_4 its reduction to chloride takes place slowly at ordinary temperatures.

The increased chemical activity of substances, when in a finely divided condition, is to be generally accounted for by the greater surface exposed, and as a rule the actions brought about are similar in kind, but differ in degree. Spongy lead appears to form no exception. Ordinary lead filings were found to reduce nitre, &c., but very much more slowly.

ADDRESS

TO THE

CHEMICAL SECTION

OF THE

BRITISH ASSOCIATION.

BY

J. H. GLADSTONE, Esq., Ph.D., F.R.S., V.P.C.S.,

PRESIDENT OF THE SECTION.

A SECTIONAL address usually consists either of a review of the work done in the particular science during the past year, or of an exposition of some branch of that science to which the speaker has given more especial attention. I propose to follow the latter of these practices, and shall ask the indulgence of my brother chemists while I endeavour to place before them some thoughts on the subject of Elements.

Though theoretical and practical chemistry are now intertwined, with manifest advantage to each, they appear to have been far apart in their origin. Practical chemistry arose from the arts of life, the knowledge empirically and laboriously acquired by the miner and metallurgist, the potter and the glass-worker, the cook and the perfumer. Theoretical chemistry derived its origin from cosmogony. In the childhood of the human race the question was eagerly put, 'By what process were all things made?' and some of the answers given started the doctrine of elements. The earliest documentary evidence of the idea is probably contained in the Shoo King, the most esteemed of the Chinese classics for its antiquity. It is an historical work, and comprises a document of still more venerable age, called 'The Great Plan, with its Nine Divisions,' which purports to have been given by Heaven to the Great Yu, to teach him his royal duty and 'the proper virtues of the various relations.' Of course there are wide differences of opinion as to its date, but we can scarcely be wrong in considering it as older than Solomon's writings. The First Division of the Great Plan relates to the Five Elements. 'The first is named Water; the second, Fire; the third, Wood; the fourth, Metal; the fifth, Earth. The nature of water is to soak and descend; of fire, to blaze and ascend; of wood, to be crooked and to be straight; of metal, to obey and to change; while the virtue of the earth is seen in seed-sowing and ingathering. That which soaks and descends becomes salt; that which blazes and ascends becomes bitter; that

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which is crooked and straight becomes sour; that which obeys and changes becomes acrid; and from seed-sowing and ingathering comes sweetness.'[1]

A similar idea of five elements was also common among the Indian races, and is stated by Professor Rodwell to have been in existence before the fifteenth century B.C., but, though the number is the same, the elements themselves are not identical with those of the ancient Chinese classic; thus, in the Institutes of Menu, the 'subtle ether' is spoken of as being the first created, from which, by transmutation, springs air, whence, by the operation of a change, rises light or fire; from this comes water, and from water is deposited earth. These five are curiously correlated with the five senses, and it is very evident that they are not looked upon as five independent material existences, but as derived from one another. This philosophy was accepted alike by Hindoos and Buddhists. It was largely extended over Asia, and found its way into Europe. It is best known to us in the writings of the Greeks. Among these people, however, the elements were reduced to four— fire, air, earth, and water—though Aristotle endeavoured to restore the 'blue ether' to its position as the most subtle and divine of them all. It is true that the fifth element, or 'quinta essentia,' was frequently spoken of by the early chemists, though the idea attaching to it was somewhat changed, and the four elements continued to retain their place in popular apprehension, and still retain it even among many of the scholars who take degrees at our universities. The claim of wood to be considered an element seems never to have been recognised in the West, unless, indeed, we are to seek this origin for the choice of the word ὕλη to signify that original chaotic material out of which, according to Plato and his school, all things were created.[2] The idea also of a primal element, from which the others, and everything else, were originated, was common in Greece, the difficulty being to decide which of the four had the greatest claim to this honour. Thales, as is well known, in the sixth century B.C. affirmed that water was the first principle of things; but Anaximenes afterwards looked upon air, and Herakleitos upon fire, while Pherekydes regarded the earth as the great ancestor, as the primal element. This notion of elements, however, was essentially distinct from our own. It was always associated with the idea of the genesis of matter rather than with its ultimate analysis, and the idea of *simple* as contrasted with *compound* bodies probably never entered into the thoughts of the contending philosophers.

The modern idea appears to have had a totally different origin, and we must again travel back to China. There, also in the sixth century B.C., the great philosopher Lao-tse was meditating on the mysteries of the world and the soul, and his disciples founded the religion of Taou. They were materialists; nevertheless they believed in a 'finer essence,' or spirit, that rises from matter, and may become a star; thus they held that the souls of the five elements, water, metal, fire, wood, and earth, arose and became the five planets. These speculations naturally led to a search after the sublimated essences of things, and the means by which this immortality might be secured. It seems that at the time of Tsin-she-hwang, the builder of the Great Wall, about two centuries before Christ, many romantic stories were current of immortal men inhabiting islands in the Pacific Ocean. It was supposed that in these magical islands was found the 'herb of immortality' growing, and that it gave them exemption from the lot of common mortals. The emperor determined to go in search of these islands, but some untoward event always prevented him.[3]

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[1] Quoted from the translation by the Rev. Dr. Legge. In that most obscure classic, the *Yî-King*, fire and water, wind and thunder, the ocean and the mountains, appear to be recognised as the elements.

[2] Students of the Apocrypha will remember the expression in the Book of Wisdom, xi. 17, 'ἡ παντοδύναμός σου χεὶρ καὶ κτίσασα τὸν κόσμον ἐξ ἀμόρφου ὕλης' ('Thy Almighty hand, that made the world of matter without form'). The same book contains two allusions to the ordinary elements, vii. 17 and xix. 18 to 20. The word στοιχεῖον is used in the New Testament only in a general sense (2 Pet. iii. 10), or in its more popular meaning of the first steps in knowledge.

[3] Nearly all my information in regard to this Taouist alchemy is derived from the writings of the Rev. Joseph Edkins, of Pekin, and the matter is treated in greater detail in an article on the 'Birth of Alchemy,' in the *Argonaut*, vol. iii. p. 1.

Some two or three centuries after this a Taouist, named Weipahyang, wrote a remarkable book called 'The Uniting Bond.' It contains a great deal about the changes of the heavenly bodies, and the mutual relation of Heaven and men; and then the author proceeds to explain some transformations of silver and water. About elixir he tells us, 'What is white when first obtained becomes red after manipulation on being formed into the elixir' ('tan,' meaning red or elixir). 'That substance, an inch in diameter, consists of the black and the white, that is, water and metal combined. It is older than heaven and earth. It is most honourable and excellent. Around it, like a wall, are the sides of the cauldron. It is closed up and sealed on every side, and carefully watched. The thoughts must be undisturbed, and the temper calm, and the hour of its perfection anxiously waited for. The false chemist passes through various operations in vain. He who is enlightened expels his evil passions, is delighted morning and night, forgets fame and wealth, comprehends the true objects of life, and gains supernatural powers. He cannot then be scorched by fire, nor drowned in water, &c. &c. . . . The cauldron is round like the full moon, and the stove beneath is shaped like the half-moon. The lead ore is symbolised by the White Tiger; and it, like metal amongst the elements, belongs to the West. Mercury resembles the sun, and forms itself into sparkling globes; it is symbolised by the Blue Dragon belonging to the East, and it is assigned to the element wood. Gold is imperishable. Fire does not injure its lustre. Like the sun and moon, it is unaffected by time. Therefore the elixir is called "the Golden Elixir." Life can be lengthened by eating the herb called Hu ma; how much more by taking the elixir, which is the essence of gold, the most imperishable of all things! The influence of the elixir, when partaken of, will extend to the four limbs; the countenance will become joyful; white hair will be turned black; new teeth will grow in the place of old ones, and age at once become youth. . . . Lead ore and mercury are the bases of the process by which the elixir is prepared; they are the hinge upon which the principles of light and darkness revolve.'

This description suggests the idea that the elixir of the Taouists was the red sulphide of mercury—vermilion—for the preparation of which the Chinese are still famous. That Weipahyang believed in his own philosophy is testified by a writer named Ko-hung, who, about a century afterwards, wrote the lives of celebrated Taouists. He tells how the philosopher, after preparing the elixir, took it, with his disciples, into a wood, and gave it first to his dog, then took it himself, and was followed by one of his pupils. They all three died, but, it appears, rose to life again, and to immortality. This brilliant example did not remain without imitators; indeed, two emperors of the Tang family are said to have died from partaking of the elixir. This circumstance diminished its popularity, and alchemy ceased to be practised in the Celestial Empire.

At the beginning of the seventh century the doctrine of Lao-tse was in great favour at the Chinese court; learning was encouraged, and there was much enterprise. At the same time the disciples of Mahomed carried their arms and his doctrines over a large portion of Asia, and even to the Flowery Land. Throughout the eighth century there were frequent embassies between eastern and western Asia, wars with the Caliphs, and even a matrimonial alliance. We need not wonder, therefore, that the teachings of the Taouist alchemists penetrated westward to the Arabian philosophers. It was at this period that Yeber-Abou-Moussah-Djafer al-Sofé, commonly called Geber, a Sabæan of great knowledge, started what to the West was a new philosophy about the transmutation of metals, the Philosopher's Stone, and the Elixir of Life; and this teaching was couched in highly poetic language, mixed with astrology and accompanied by religious directions and rites. He held that all metals were composed of mercury, sulphur, and arsenic, in various proportions, and that the noblest metal could be procured only by a very lengthy purification. It was in the salts of gold and silver that he looked for the Universal Medicine. Geber himself was an experimental philosopher, and the belief in transmutation led to the acquirement of a considerable amount of chemical knowledge amongst the alchemists of Arabia and Europe. This gradually brought about a conviction that the three reputed elementary bodies, mercury, sulphur, and

salt or acid, were not really the originators of all things. There was a transition period, during which the notion was itself suffering a transmutation. The idea became gradually clearer that all material bodies were made up of certain constituents, which could not be decomposed any further, and which, therefore, should be considered as elementary. The introduction of quantitative methods compelled the overthrow of mediæval chemistry, and led to the placing of the conception of simple and compound bodies upon the foundation of scientific fact. Lavoisier, perhaps, deserves the greatest credit in this matter, while the labours of the other great chemists of the eighteenth and the beginning of the nineteenth centuries were in a great measure directed to the analysis of every conceivable material, whether solid, liquid, or gaseous. These have resulted in the table of so-called elements, now nearly seventy in number, to which fresh additions are constantly being made.

Of this ever-growing list of elements not one has been resolved into simpler bodies for three-quarters of a century; and we, who are removed by two or three generations from the great builders of our science, are tempted to look upon these bodies as though they were really simple forms of matter, not only unresolved, but unresolvable. The notation we employ favours this view and stamps it upon our minds.

Is it, however, a fact that these reputed elements are really simple bodies? or, indeed, are they widely different in the nature of their constitution from those bodies which we know to be chemical compounds? Thus, to take a particular instance, are fluorine, chlorine, bromine, and iodine essentially distinct in their nature from the compound halogens, cyanogen, sulphocyanogen, ferricyanogen, &c.? Are the metals lithium, sodium, and potassium essentially distinct from such alkaline bases as ammonium, ethylamine, di-ethylamine, &c.? No philosophical chemist would probably venture to answer this question categorically with either 'yes' or 'no.' Let us endeavour to approach it from three different points of attack—(1) the evidence of the spectroscope, (2) certain peculiarities of the atomic weights, and (3) specific refraction.

1. *The Spectroscope.*—It was at first hoped that the spectroscope might throw much light upon the nature of elements, and might reveal a common constituent in two or more of them; thus, for instance, it was conceivable that the spectrum lines of bromine or iodine vapour might consist of the rays given by chlorine *plus* some others. All expectations of this have hitherto been disappointed: what we do frequently find is a certain similarity of character among the spectra of analogous elements, not rays of identically the same refrangibility. Yet, on the other hand, it must not be supposed that such a negative result disproves the compound nature of elements, for as investigation proceeds it becomes more and more clear that the spectrum of a compound is not made up of the spectra of its component parts.

Again, the multiplicity of rays given out by some elements, when heated, in a gaseous condition, such as iron, has been supposed to indicate a more complex constitution than in the case of those metals, such as magnesium, which give a more simple spectrum. Yet it is perfectly conceivable that this may be due to a complexity of arrangement of atoms all of the same kind.

Again, we have changes of a spectrum at different temperatures; new rays appear, others disappear; or even there occurs the very remarkable change from a fluted spectrum to one of sharp lines at irregular intervals, or to certain recurring groups of lines. This, in all probability, does arise from some redistribution, but it may be a redistribution in a molecular grouping of atoms of the same kind, and not a dissociation or rearrangement of dissimilar atoms.

A stronger argument has been derived from the revelations of the spectroscope in regard to the luminous atmospheres of the sun. There we can watch the effect of heat enormously transcending that of our hottest furnaces, and of movements compared with which our hurricanes and whirlwinds are the gentlest of zephyrs. Mr. Lockyer, in studying the prismatic spectra of the luminous prominences or spots of the sun, has frequently observed that on certain days certains lines, say of the iron spectrum, are non-existent, and on other days certain other lines disappear, and that in almost endless variety; and he has also remarked that occasionally cer-

tain lines of the iron spectrum will be crooked or displaced, thus showing the vapour to be in very rapid motion, while others are straight, and therefore comparatively at rest. Now, as a gas cannot be both at rest and in motion at the same time and the same place, it seems very clear that the two sets of lines must originate in two distinct layers of atmosphere, one above the other, and Mr. Lockyer's conclusion is that the iron molecule was dissociated by heat, and that its different constituents, on account of their different volatility, or some other cause, had floated away from one another. This seems to me the easiest explanation of the phenomenon; and, as dissociation by heat is a very common occurrence, there is no *a priori* improbability about it. But we are not shut up to it, for the different layers of atmosphere are certainly at different temperatures, and most probably of different composition. If they are of different temperatures the variations of the spectrum may only be an extreme case of what must be acknowledged to be a fact by everyone more or less—that bodies emit, or cease to emit, different rays as their temperature increases, and notably when they pass from the liquid to the gaseous condition. And again, if the composition of the two layers of atmosphere be different, we have lately learnt how profoundly the admixture of a foreign substance will sometimes modify a luminous spectrum.

2. *Peculiarities of Atomic Weights.*—At the meeting of this Association at Ipswich, in 1851, M. Dumas showed that in several cases analogous elements form groups of three, the middle one of which has an atomic weight intermediate between those of the first and third, and that many of its physical and chemical properties are intermediate also. During the discussion upon his paper, and subsequently,[1] attention was drawn to the fact that this is not confined to groups of three, but that there exist many series of analogous elements having atomic weights which differ by certain increments, and that these increments are in most cases multiples of 8. Thus we have lithium, 7; sodium, 23, *i.e.* 7 + 16; potassium, 39, *i.e.* 7 + (16 × 2); and the more recently discovered rubidium, 85, *i.e.* 7 + (16 × 5) nearly; and cæsium, 133, *i.e.* 7 + (16 × 8) nearly. This is closely analogous to what we find in organic chemistry, where there are series of analogous bodies playing the part of metals, such as hydrogen, methyl, ethyl, &c., differing by an increment which has the atomic weight 14, and which we know to be CH_2. Again, there are elements with atomic weights nearly the same or nearly multiples of one another, instances of which are to be found in the great platinum group and the great cerium group.[2] This suggests the analogy of isomeric and polymeric bodies. There is also this remarkable circumstance: the various members of such a group as either of those just mentioned are found together at certain spots on the surface of the globe, and scarcely anywhere else. The chemist may be reminded of how in the dry distillation of some organic body he has obtained a mixture of polymerised hydrocarbons, and may perhaps be excused if he speculates whether in the process of formation of the platinum or the cerium group, however and whenever it took place, the different elements had been made from one another and imperfectly polymerised.

But this is not the largest generalisation in regard to the peculiarities of these atomic weights. Newlands showed that, by arranging the numbers in their order, the octaves presented remarkable similarities, and, on the same principle, Mendelejeff constructed his well-known table. I may remind you that in this table the atomic weights are arranged in horizontal and vertical series, those in the vertical series differing from one another, as a rule, by the before-mentioned multiples of 8—namely 16, 16, 24, 24, 24, 24, 32, 32—the elements being generally analogous in their atomicity and in other chemical characters. Attached to the elements are figures, representing various physical properties, and these in the horizontal series appear as periodic functions of the atomic weights. The table is incomplete, especially in its lower portions, but, with all its imperfections and irregularities, there can be no doubt that it expresses a great truth of nature. Now, if we were to interpolate the compound bodies which act like elements—methyl, 15; ammonium, 18; cyanogen, 26—into

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[1] *Phil. Mag.*, May 1853.

[2] Another curious instance is the occurrence of nickel and cobalt in all meteoric irons, with occasionally chromium or manganese, the atomic weights and other properties of which are very similar.

Mendelejeff's table, they would be utterly out of place, and would upset the order both of chemical analogy and of the periodicity of the physical properties.

3. *Specific Refraction.*—The specific refraction has been determined for a large majority of the elements, and is a very fundamental property, which belongs to them apparently in all their combinations, so long at least as the atomicity [1] is unchanged. If the figures representing this property be inserted into Mendelejeff's table, we find that in the vertical columns the figures almost invariably decrease as the atomic weights increase. If, however, we look along the horizontal columns, or better still if we plot the figures in the table by which Lothar Meyer has shown graphically that the molecular volume is a periodic function of the atomic weights, we shall see that they arrange themselves in a series of curves similar to but not at all coincident with his. The observations are not so complete or accurate as those of the molecular volumes, but they seem sufficient to establish the fact, while the points of the curves would appear to be, not the alkaline metals, as in Meyer's diagram, but hydrogen, phosphorus and sulphur, titanium and vanadium, selenium, antimony. Now, if we were to insert the specific refractions of cyanogen, ammonium, and methyl into this table, we should again show that it was an intrusion of strangers not in harmony with the family of elements.

But there is another argument to be derived from the action of light. The refraction equivalent of a compound body is the sum of the refraction equivalents of its compounds; and, if there is anything known for certain in the whole subject, it is that the refraction equivalent of an organic compound advances by the same quantity (7·6) for every increment of CH_2. If, therefore, the increment between the different members of a group of analogous elements, such as the alkaline metals, be of the same character, we may expect to find that there is a regular increase of the refraction equivalent for each addition of 16. But this is utterly at variance with fact : thus, in the instance above quoted, the refraction equivalent of lithium being 3·8, that of sodium is 4·8, of potassium 8·1, of rubidium 14·0, and of cæsium about 13·7. Neither does the law obtain in those series in which the increment is not a multiple of 8, as in the case of the halogens, where the increment of atomic weight is 45, and the refraction equivalents are chlorine 9·9, bromine 15·3, and iodine 24·5.

The refraction equivalents of isomeric bodies are generally identical ; and the refraction equivalents of polymeric bodies are in proportion to their atomic weights. Among the groups of analogous elements of the same, or nearly the same, atomic weight we do find certain analogies : thus cobalt and nickel are respectively 10·8 and 10·4, while iron and manganese are respectively 12·0 and 12·2. But, as far as observation has gone at present, we have reason to conclude that, if metals stand to one another in the ratio of 2 : 1 in atomic weight, their refraction equivalents are much nearer together than that; while, on the other hand, the equivalent of sulphur, instead of being the double of that of oxygen, is at least five times as great.

The general tendency of these arguments is evidently to show that the elementary radicals are essentially different from the compound radicals, though their chemical functions are similar.

There remains still the hypothesis that there is a 'primordial element,' from which the others are derived by transmutation. With the sages of Asia it was the 'blue ether,' with Thales water, with Dr. Prout hydrogen. The earlier views have passed away, and the claims of hydrogen are being fought out by some of our ablest analysts on the battlefield of atomic weights and their rigorous determination.

There does not appear to be any argument which is fatal to the idea that two or more of our supposed elements may differ from one another rather in form than in substance, or even that the whole seventy are only modifications of a prime element ; but chemical analogies seem wanting. The closest analogy would be if

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[1] This exception includes not merely such changes as that from a ferrous to a ferric salt, but the different ways in which the carbon is combined in such bodies as ethene, benzene, and pyrene.

we could prepare two allotropic conditions of some body, such as phosphorus or cyanogen, which should carry their allotropism into all their respective compounds, no compound of the one form being capable of change into a compound of the other. Our present knowledge of allotropism, and of variations in atomicity, affords little, if any, promise of this.

The remarkable relations between the atomic weights of the elements, and many peculiarities of their grouping, force upon us the conviction that they are not separate bodies created without reference to one another, but that they have been originally fashioned, or have been built up from one another, according to some general plan. This plan we may hope gradually to understand better; but if we are ever to transform one of these supposed elements into another, or to split up one of them into two or three dissimilar forms of matter, it will probably be by the application of some method of analysis hitherto unknown.

Nothing can be of greater promise than the discovery of new methods of research; hence I need make no apology to others who have lately done excellent work in chemistry if I single out the Bakerian Lecture of this year, by Mr. Crookes, on 'Radiant Matter Spectroscopy.' It relates to the prismatic analysis, not of the light transmitted or absorbed in the ordinary way by a solid or liquid, nor of that given out by incandescent gas, but the analysis of the fluorescence that manifests itself in certain bodies when they are exposed to an electric discharge in a highly exhausted vacuum. He describes, in an interesting and even amusing manner, his three years' quest after the origin of a certain citron band, which he observed in the spectrum of the fluorescence of many substances, till he was led into that wonderful labyrinth of uncertain elements which are found together in samarskite, and eventually he proved the appearance to be due to yttrium. As the test is an extremely delicate one, he has obtained evidence of the very general dissemination of that element, in very minute quantities—and not always very minute, for the polypes that built up a certain pink coral were evidently able to separate the earth from the sea water, as their calcareous secretion contained about $\frac{1}{2}$ per cent. of yttrium. We have reason to hope that this is only the first instalment of discoveries to be made by this new method of research.
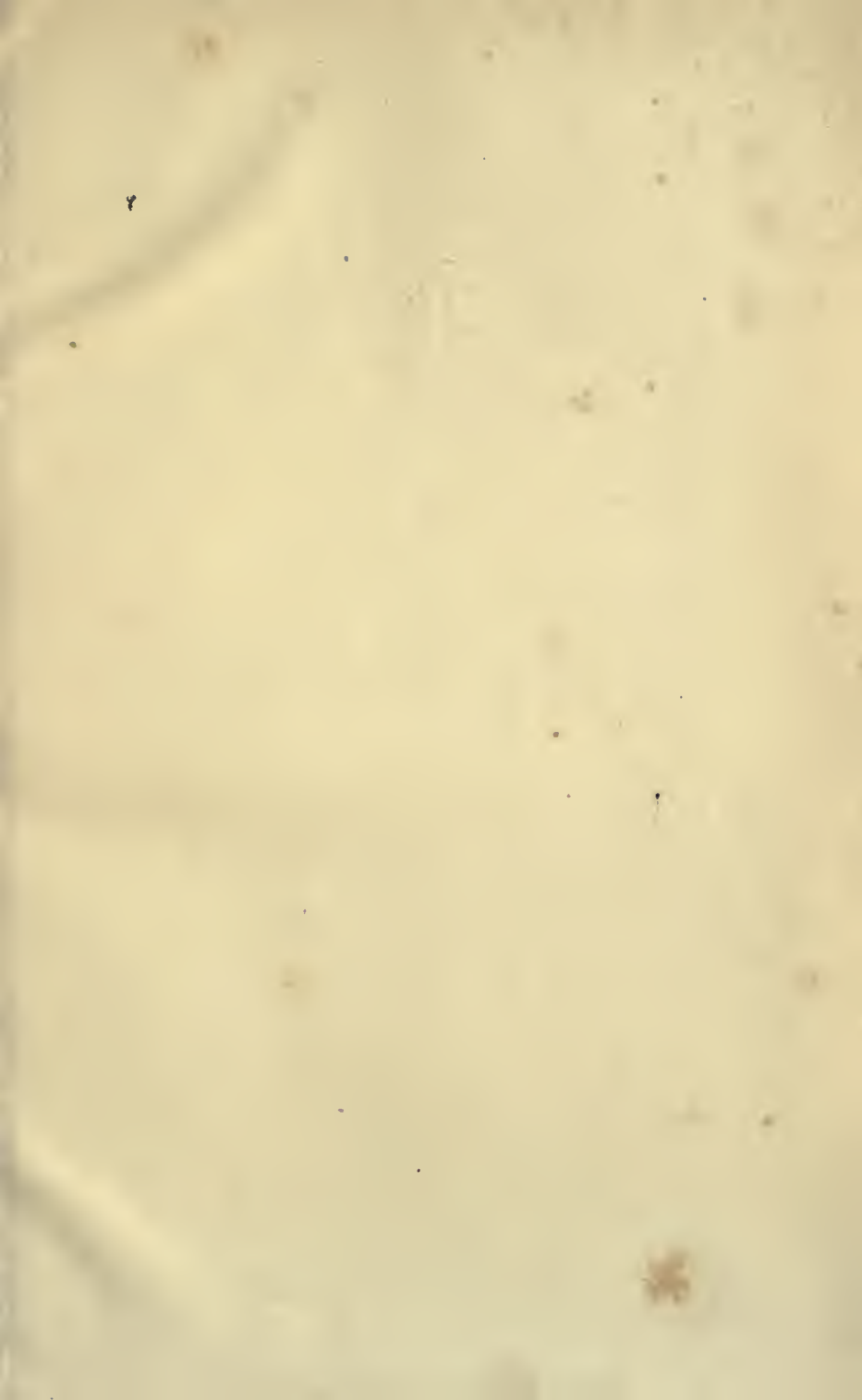
I cannot conclude without a reference to the brightening prospects of technical chemistry in this country. I do not allude to the progress of any particular industry, but to the increased facilities for the education of those engaged in the chemical manufactures. First as to the workpeople. Hitherto the young artisan has had little opportunity of learning at school what would be of the greatest service to him in his after career. The traditions of the Middle Ages were all in favour of literary culture for the upper classes, and the education suited for these has been retained in our schools for the sons of the people. It is true that some knowledge of common things has been given in the best schools, and the Education Department has lately encouraged the teaching of certain sciences in the upper standards. In the Mundella Code, however, which came into operation last year, 'elementary science' may receive a grant in all the classes of a boys' or girls' school, and in the suggested scheme there is mentioned simple lessons on 'the chemical and physical principles involved in one of the chief industries of England, among which Agriculture may be reckoned,' while 'Chemistry' is inserted among 'the specific subjects of instruction' that may be given to the older children. It is impossible, as yet, to form an estimate of the extent to which managers and teachers have availed themselves of this permission, for the examinations of her Majesty's inspectors under the new code have only just commenced; but one of the best of the Board schools in London has just passed satisfactorily in chemistry both with boys and girls. I trust that in those parts of the country where chemical industries prevail chemistry may be largely taken up in our elementary schools.

The great deficiency in our present educational arrangements is the want of the means of teaching a lad who has just left the common school the principles of that industry by which he is to earn his livelihood. The more purely scientific chemistry, however, may be learnt by him now in those evening classes which may be formed under the Education Department, as well as in those that have long been established under the Science and Art Department. The large amount of

attention that is now being given to the subject of technical education is creating in our manufacturing centres many technical classes and colleges for students of older growth.

As to inventors, and the owners of our chemical factories, in addition to the Chemical Society and the Chemical Institute, there has recently been founded the Society of Chemical Industry. It came into existence with much promise of success; at the close of its second year it numbered 1,400 members; it has now powerful sections in London, Manchester, Liverpool, Newcastle, and Birmingham; and it diffuses information on technical subjects in a well-conducted monthly journal.

May the abstract science and its useful applications ever prove helpful to one another, and become more and more one chemistry for the benefit of mankind.